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THE CHEMICAL NEWS, JULY 27, 1917

THE
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AND

JOURNAL OF PHYSICAL SCIENCE.

WITH WHICH IS INCORPORATED THE "CHEMICAL GAZETTE."

A Journal of Practical Chemistry

IN ALL ITS APPLICATIONS TO

PHARMACY, ARTS, AND MANUFACTURES.

EDITED BY

SIR WILLIAM CROOKES, O.M., D.Sc., F.R.S., &c.

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No. 2980.—JANUARY 5, 1917.

SYNTHETIC CHEMISTRY AND THE RENASCENCE OF BRITISH CHEMICAL INDUSTRY.*

By Prof. GILBERT T. MORGAN, F.R.S.

IN attempting at very short notice to deliver this Inaugural Address it becomes my pleasant duty to congratulate the Chemical Society of the Royal College of Science on reaching its twenty-first anniversary. This year the Society attains its majority, for it was founded by our Emeritus Professor, Sir William Tilden, in the autumn term of 1895. It was my privilege to be a foundation member and to serve on the first committee. Moreover, I had the honour of reading the first paper before the Society; this communication being entitled "Artificial Colouring Matters."

The intervening twenty-one years have brought many changes, both to individuals and to the college. In 1907 the chemical department left the old buildings in Exhibition Road and took up its abode in the palatial edifice opposite the Imperial Institute. Affiliation of the Royal College of Science with the Imperial College of Science and Technology led to further developments in the direction of applied chemistry. These developments would doubtless have proceeded along evolutionary lines when the war came to alter radically in all directions our ideas concerning the relative importance of the value of various scientific pursuits. "It's an ill wind that blows no one any good," and the war has so far done British chemical workers one good turn in demonstrating their supreme national importance to an apathetic public. This recognition, although not so complete or so generous as it might be, is nevertheless very manifest.

From the chemical departments of this and other colleges of science hundreds of the most public spirited and most enterprising students have gone into the ranks of the special brigade of the Royal Engineers, into explosive works, and into other factories dealing with munitions of war. Many have made the supreme sacrifice for their country's cause, and their survivors are all working willingly and cheerfully under very trying circumstances.

Synthetic Chemistry and National Defence.

In the early days of the war the favourite catch phrase was "Business as usual," and arising out of this preposterous ideal came the first chemical crisis. It was speedily found that a vast business in textiles and other important products having an annual output of

£200,000,000 sterling could not be carried on as usual owing to stoppage in the supply of German dyes. Considerable enterprise and capital, both private and governmental, were diverted towards establishing means for coping with the dye famine. The situation at present is much easier, but considerable leeway has still to be made before our dye producers can hope to face German competition on equal terms. Considering the many adverse circumstances remarkable progress has been made. Dyes are now being manufactured of which, at the outbreak of war, nothing was known beyond the designedly incomplete details of patent specifications filed by the German discoverers and makers.

It is worthy of note that Great Britain was not alone in this quandary as regards dyes and their intermediate products. Other dye-using nations, such as France, Italy, Russia, the United States, and Japan, had all been dependent on German supplies, and have had to adopt equally strenuous means to produce dyes for themselves.

Another circumstance has arisen out of the war which makes it certain that all progressive industrial nations will make every effort to develop a home production of colouring matters. The urgency of this matter lies in the fact that a well organised coal-tar products industry is an essential part of any modern scheme for national defence. The second chemical war crisis arose over the shortage of high explosives. This shortage, which existed among the Allies only and not in the two Central European Powers, was due to lack of enterprise in the working up of coal-tar products. What had long been known to expert chemists was ignored by the allied nations and their Governments, namely, that the coal tar products are not only the basis of synthetic dyes but also of high explosives. Accordingly, a nation destitute of the coal tar industry cannot nowadays be self contained and independent in matters of national defence. Such a nation can only furnish men; their ammunition must be obtained elsewhere from allies or neutrals. In the first year of the war, while the Allies were all more or less in this predicament, Germany was able swiftly to divert the extensive plants of her huge colour factories to the manufacture of high explosives.

The interdependence of these two branches of chemical manufacture, high explosives and synthetic dyes, is, therefore, of cardinal importance in considering the prospects of industrial chemistry as a career for scientifically trained men and women.

It is fashionable at present to think that the domain of coal-tar chemistry has again become the Tom Tiddler's ground which it was during the epoch ushered in by the discoveries of Perkin (1856) and Verguin (1859), who prepared respectively mauve or aniline purple and magenta

* The Inaugural Address to the Royal College of Science Chemical Society for the Session 1916-17.

or aniline red. It is true that behind the barrage of the naval blockade tremendously inflated prices are being obtained for quite ordinary dyes, so that any chemist with a small capital devoted to the manufacture of one or two coal-tar specialities can reasonably expect to gain a very high return for his outlay. Moreover, the needs of the larger firms engaged in dye production or in the manufacture of high explosives are so great that their principals are willing to take into their employment almost anyone who can wave a test-tube in a Bunsen burner, the rates of remuneration being considerably higher than those offered before the war to well-trained chemical graduates.

These halcyon days for the coal-tar chemist will not continue very long after the cessation of hostilities. Since it has been proved to the hilt that a well organised coal-tar industry is essential for purposes of national defence, one may assume with considerable confidence that the leading nations of the world will each cultivate to the utmost the manufacture of coal-tar products, including dyes. Consequently the dye users will be largely supplied by dye-makers of the same nationality. Only dyes of superlative quality or exceptional properties will find foreign markets across the various tariff walls. Competition for the neutral markets of non-producers will be as severe as ever it was before the war. Success will come to those dye-makers and to those producers of other fine chemicals who will use the most scientific methods of investigation and development. These advantages can be secured only by the employment of large staffs of well-trained chemists.

Hopes are being entertained in this country that the trade in fine chemicals will be fostered and protected by a boycott of German products. This idea is as fallacious psychologically as it is economically. For a long time after the war Germans will be very unpopular among peoples of the Allied nations, who will be averse to social intercourse with them. But this sentiment will not suffice to hinder trading relationships. If enemy manufacturers have something desirable for sale they will get it sold. The only way to boycott German goods is to improve on them in either quality, price, or both. The following hypothetical cases may serve to crystallise opinion. German chemists and chemico-therapeutists excel in the production of useful synthetic drugs, and already before the war Wassermann had announced that certain preparations of selenium and tellurium appeared to have a restrictive action on malignant tumours. It is, at least, quite conceivable that German workers may be the first to hit upon a cure for cancer. Are we going to see our dearest relatives and our best friends die of this scourge when they might be saved by a German remedy? Similarly, it may be found in the future that the retention of our great textile industries might depend on the use of some German dyeing process. In such a case it would be national suicide not to utilise the invention, even though of enemy origin.

College Training of Industrial Chemists.

I believe that in the future the prizes of the chemical profession will be greater, but the competition keener than has hitherto been the case. How then should the chemical student prepare for the strenuous struggle? His training should be centred on obtaining a wide practical knowledge of analytic and synthetic chemistry. It is unnecessary that the student should specialise while at college in the branch to which he will afterwards devote himself in the works or research laboratory, but it is essential that his training should have given him that particularly chemical outlook which is sometimes called "the chemical instinct." Throughout his college career the chemical student should strive at increasing perfection in the art of preparing, purifying, and analysing chemical compounds and their component elements. He should become acquainted with the physical properties of these chemical substances and the employment of these proper-

ties in the identification, separation, and purification of chemical entities. So far as time permits he should learn something of the industrial application of these materials. But all this work should be carried out from the standpoint of molecular constitution, and the student should accustom himself to visualise in space the arrangements assumed to obtain in the molecules of the substances under examination.

Three or four years of this training should endow the chemical student with a liberal measure of the laboratory arts. He should be ready to make the most difficult preparation with the utmost economy of time and material and should be able to identify his products with precision by analysis or other methods of physical or chemical diagnosis.

Since the object of this college training is to produce a chemist capable of initiating the manufacture of chemical products on a commercial scale, it has been suggested that the student's work should include courses on engineering and machine design. This addition would certainly render more harmonious the future relations of the industrial chemist with his works' colleague, the engineer. But even assuming that the student spent eight years over his college training, taking the first four years in chemistry and the second four in engineering, or *vice versa*, it is very improbable that he would become endowed with the dual set of qualifications which would justify his designation as a chemical engineer. By a chemist I mean a scientific worker who can undertake original research in chemistry. Similarly, an engineer is one who is qualified to apply his originality to problems of engineering. It is very rarely that one finds an individual so gifted as to be able to undertake, with any reasonable chance of success, original investigations in both these fields of scientific activity. The so-called chemical engineer is very frequently a chemist among engineers and an engineer among chemists: Jack of both trades; master of neither.

The difference between chemist and engineer is far deeper than any differentiation induced by training; it is temperamental.

The chemist and engineer represent two entirely different types of mind, the analytical and the constructional. To the individual possessed of the former mental attributes a year spent in chemical research would be far more beneficial than one spent in engineering. The research year would develop still further his chemical instinct; the same period devoted to machine design or to mechanical problems would not convert him into an engineer.

In Germany the research qualification has always been regarded as essential to the attainment of a chemical degree. Here in this country a lot of nonsense has been talked and written about the undesirability of synthetic researches leading to the addition of new compounds to an already swollen total of known chemical substances.

This objection, which is stated with uncompromising frankness in the following passage taken from an English work on organic chemistry published a few years ago, represents what I term Malthusian chemistry, a school of chemical thought which supposes that progress in chemistry is best attained by restricting the output of new chemical compounds.

"Since the time of Kekulé organic chemistry has been for the most part a synthetic science. At the present day considerably over a hundred thousand organic compounds are known, and one need not have the least hesitation in saying that if 70 per cent of them had never been synthesised we should not feel the lack of them to any appreciable extent. The reason for this enormous flood of synthetic material is to be found in the German University system; for since, under the German regulations the degree in chemistry is granted only on the results of original research, it follows that every Ph.D. represents so many new compounds—at least, as a general rule. But these do not include all the forces leading to the steady pursuit of the synthetic branch. The great German dye industry employs in itself an army of chemists, and from

them also flows a steady stream of new compounds. The same may be said of the explosive manufacturers and the firms which produce synthetic drugs."

The creed of Malthusian chemistry has obtained so much support among British chemists that it is worth while to analyse the quoted passage with the object of disclosing its fallacies.

It may first be asked why have German Universities—as a general rule—decided to give the Ph.D. degree in chemistry to candidates working through an "Arbeit" which represents crudely so many new compounds? The answer is that as a result of long experience the German chemical authorities have decided that this system is the best way of teaching a young chemist his job. The particular group of substances selected is immaterial. At one University it will be polypeptides, at another unsaturated fatty acids, at a third organic arsenicals, at a fourth the colouring matters of flowers, and so on. The utility of the system is that the candidate for the doctorate is receiving a thorough training in the laboratory arts. He learns a great deal about chemical synthetic processes, oxidation, reduction, halogenation, hydrolysis, and many other diverse types of condensation and general reactions. He has to make use of different processes for separating and purifying synthetic products, checking the result of his work by appropriate analytic methods. Over 90 per cent of the successful candidates are destined to take up posts, either in the large coar-tar colour works or in other factories dealing with fine chemicals. Their academic training carried out in the manner just mentioned fits them for their life work in a chemical factory where the output of new substances continues at an accelerated speed. The answer to the enquiry why should this be so is very simple. In the long run it pays chemical factories to prepare and examine hundreds of new substances. Occasionally a new product arises with useful properties, and then the sale of this substance pays with a good margin of profit for all the expensive researches lavished on the other substances.

The following table, compiled by Dr. Wahl, the eminent French expert on colour chemistry, shows that it pays to employ large staffs of chemists, who are employed chiefly in making new compounds:—

	No. of chemists.	No. of employees.	Dividends paid, per cent.						
	1900.	1900.	1897.	1900.	1905.	1909.	1910.	1911.	
Badische Aniline and Soda Factories	148	8640	24	24	22	24	24	25	
Colour Works of Meister, Lucius, and Brünig	120	3555	26	26	27	27	27	30	
Colour Factories of F. Bayer	145	7889	18	18	24	24	—	29	
Berlin Aniline Company	55	1800	12½	15	18	18	—	20	

The discovery that phenyldimethyl-iso-pyrazolone (anti-pyrene) had useful physiological properties was an accident. The firm of Meister, Lucius, and Brünig, who exploited this invention, must have spent large sums in researches on the pyrazolone series. Out of these they obtained another useful compound—the drug, pyramidodimethylamino-anti-pyrene—and the profits on the sales of these two medicaments more than recompensed them for their outlay.

It may be said that much of this synthetic work is inaccurate and superficial. That criticism may be levelled against pioneers in all branches of human endeavour. Explorers, who risk health and fortune and frequently give their lives, in disclosing the secrets of hidden continents, are not always topographically impeccable, but their enterprise paves the way for more cautious and accurate cartographers. The work of pioneers is essential and its crudities are atoned by daring and originality.

(To be continued).

GRAIN-GROWTH IN DEFORMED AND ANNEALED LOW CARBON STEEL.*

By RALPH H. SHERRY, M.A.

CONSIDERABLE attention has been given in recent years to the phenomenon of coarse crystallisation or grain-growth in pure iron and low-carbon steels permanently deformed and annealed. While grain-growth may occur in certain other metals and homogeneous alloys, under similar conditions, iron is worthy of special attention because of certain physical properties influencing grain-growth which it possesses, and more particularly because of its extensive use commercially.

Not a little difficulty has faced workers in such materials as sheet, wire, cold-drawn bar stock, and pressings of low carbon steel. From time to time mysterious epidemics of brittleness in the material would be encountered, breakage occurring under ridiculously small stresses, accompanied by coarsely grained fractures. Annealing often seemed to aggravate the difficulty. Material which passed safely through the various fabricating processes was often put into service under a shroud of fear that it would "crystallise in service."

Fortunately, most of the factors determining these irritating conditions have gradually become known, and it is the purpose of this paper to state the results of a rather extended investigation covering the subject, and to explain the conditions under which grain-growth occurs. Methods will be suggested by which this trouble may be prevented or cured in general, and for each material investigated in particular, and general conclusions with regard to the phenomenon noted in the investigation will be given.

Historical.

The occurrence of coarse crystallisation in low-carbon steel at low temperatures was first mentioned by Stead (*Journal of the Iron and Steel Institute*, 1898, i., 145), who observed it "in certain steels and pure irons, originally of fine grain, produced by forging or certain heat treatment," when annealed between 500° C. (930° F.) where slow growth occurred, and at 600–750° C. (1110–1380° F.), where the growth was more rapid. Annealing at 700° C. (1290° F.) for a few hours produced exceedingly coarse grains. Grain-growth was also observed in sheets containing 0.05–0.12 per cent carbon. One peculiarity noted was that grain-growth was never observed in sheets of a gauge less than 18 (Stead, *Idem*, 1898, ii., 137). Experiments to produce the structure at will were not invariably successful.

Charpy (*Comptes Rendus*, cli.) showed that a coarse granular structure could be produced in steel low in carbon and phosphorus by pressing the material in a screw plate, and subsequently annealing at 700° C. (1290° F.). He obtained grains about ten times the original size; by proper selection of the annealing temperature and time extremely large grains could be produced.

Sauveur produced the same condition in low carbon steel, deforming the metal by tension, compression, bending, and in the Brinell hardness testing machine, subsequently annealing his specimens below the thermal critical range ("Note on the Crystalline Growth of Ferrite below its Thermal Critical Range," *Proc. Sixth International Congress for Testing Materials*, 1912, vol. xi.). The existence of three zones of crystallisation corresponding to the amount of strain was observed. Sauveur came to the conclusion that a definite or "critical" strain was necessary in order to produce grain-growth on annealing. In other investigations the strain necessary to produce grain-growth has been found to cover a rather wide range. The narrow limits noted by Sauveur are probably due to his use of annealing temperatures altogether below the thermal critical range.

Chappell (*Journ. Iron and Steel Inst.*, 1914, i., 460) investigated the phenomenon in somewhat the same way

* A Paper read before the Faraday Society, December 18, 1916.

as Sauveur by means of Brinell impressions and by pressing, by gradual stages, a single groove along the centre of a bar and sectioning the bar along the groove. (A very complete bibliography of the subject of the deformation of iron will be found in Chappell's article). For greater convenience in handling, grooves were also impressed at intervals across the bar. These bars were heated at one end in a furnace, the other end being kept cool in the air, care being taken to insure a regular fall of temperature along the bar, thus permitting the study of the temperature variable. In order to determine the quantitative effect of deformation, tension to fracture was applied to tapered bars, which were then annealed at various temperatures. The effect of deformation at high temperatures was investigated, and exceedingly coarse grains produced by subjecting the material to stress at 870°C . (1600°F .), and then annealing at about 850°C . (1560°F .). No occurrence of coarse crystallisation was noted in annealed cold-drawn wire, this condition being produced only in pure iron that had received local deformation. It is stated, however, that the negative result is probably due to the wire having been strained beyond the limiting range. The effect of bending under shock was also tested. In cases of local deformation Chappell notes the existence of three zones after annealing within a certain range; one representing a high degree of deformation in which there is no appreciable change in the crystals, a central zone of moderate deformation in which there is a large crystalline growth, and a third zone of little or no deformation in which there is no growth, a result which corresponds closely to that obtained by Sauveur. It is stated that the highly deformed inner zone is not one in which no change takes place on annealing, but a zone in which the recrystallisation takes place at a lower temperature than that of the outer zone. With regard to the quantitative effect of deformation and the temperatures within which recrystallisation occurs, Chappell states that "plastic strain in practically every degree produced recrystallisation on annealing below A_3 ," and also that, "given sufficient time the major part of the recrystallisation is complete at $700-750^{\circ}\text{C}$., and in its incipient stages may commence as low as 350°C ."

The influence of carbon, according to the investigation, is to restrict the size of the crystals developed, and to make a higher degree of stress necessary to produce growth, and also to lower the temperature at which the gross crystallisation is destroyed. This conclusion was arrived at as a result of the examination of a bar of 0.30 per cent carbon steel, which was turned down into a double cone-shaped test-piece, similar to the tapered tensile test-pieces mentioned. This bar was then partially decarbonised by ore annealing, and after cooling was pulled to fracture and sectioned down the centre. One half was then heated at progressively higher temperatures between 600° and 900°C . by 50° intervals, thus permitting a study of the effect of the three variables, carbon, strain, and temperature, with one test-piece.

Some years ago the writer had occasion to investigate the occurrence of coarse crystallisation in low-carbon steel in various commercial forms, and published a brief account of part of this work (Sherry, "Metallurgical and Chemical Engineering," October, 1912, p. 666). This investigation has been continued with several commercial varieties of cold-worked low-carbon steel, largely under commercial conditions.

The materials investigated were hot-rolled rod, cold-drawn wire, hot- and cold-rolled sheet, cold-rolled strip, cold-drawn tubing and pressings, the principal commercial forms of low-carbon steel in which coarse crystallisation occurs. The effects of forging hot and cold were investigated on a small scale by the use of a hand hammer on small test-pieces. The quantitative effect of permanent deformation received special attention.

Conditions under which Grain-growth occurs.

The formation of coarse grains in low-carbon steel will follow the action of a limited amount of stress exceeding

the elastic limit, or, in other words, limited permanent deformation, and subsequent annealing within certain temperature ranges. This has been confirmed by all investigators of this phenomenon. In the writer's earlier investigations certain other phenomena depending upon the quantitative effect of permanent deformation were observed, and have been confirmed by the later investigations. On varying by narrow steps the amount of applied stress within the range mentioned, it was noted that the less the permanent deformation the greater was the grain-size on subsequent annealing. Within the limiting range of strain and near the lower limit there seems to be a definite or "critical" strain, below which the range of temperature within which grain-growth will occur is limited by the A_1 , A_2 thermal critical points, about 690° and 780°C . (1275° and 1435°F .). When the material is strained beyond this point, the annealing range is considerably extended, falling between about 650° and 900°C . (1200° and 1650°F .). The moderate grain-growth occurring below 650°C . (1200°F .) noted by other investigators was not found in this investigation. This "critical" strain mentioned has not been definitely observed by other investigators, although Chappell's statement mentioned (that the highly deformed inner zone is not one in which no change takes place on annealing, but a zone in which the recrystallisation takes place at a lower temperature than that of the outer zone) may be taken as partial confirmation of its existence. The quantitative effect of strain on the grain-size has also been partly confirmed by Chappell's work.

Standards of Measurement.

In order to study the effect of permanent deformation quantitatively it was necessary to find some fairly accurate and convenient standard of measurement, direct if possible, but at least relative. Measurement of the stress applied beyond the elastic limit is of course direct, but is applicable only when applied in tension or compression in such a way that this may be determined, and, in commercial cases particularly, offers neither a convenient nor a practical standard. On this account the more convenient and relatively accurate reduction of area was adopted. This can be determined easily and with reasonable accuracy in a large number of commercial operations, as, for instance, the rolling of strip steel or the drawing of wire, where the measurement of the applied tensile stress would be impossible. As it is necessary to exceed the elastic limit in order to produce grain-growth, the reduction of area, with its origin at the elastic limit, is also a more relatively accurate standard of measurement. In certain cases, of which some pressing operations to be discussed are typical, the nature of the strain may be so complicated that no simple standard of measurement will serve to define it, and some purely relative and empirical standard must be adopted. In many such cases, however, the reduction of area will serve as a basic standard.

Experimental Operations.

Forging and Hot Rolling.—A number of samples of hot-rolled rod of about half inch diameter, found to be fine-grained after annealing within the critical range, were forged under widely varying conditions, annealed, and examined. The forging was carried on by means of a hand hammer, and all the samples were finally annealed at 700°C . (1290°F .). Certain samples were heated to temperatures above 900°C . (1650°F .) and hammered; the temperature at which work ceased was estimated by some approximate means, such as colour in semi-darkness or by the scorching effect on wood. Other samples were hammered cold. Where grain-growth was found it was usually confined to a narrow area about one-sixteenth inch wide at the periphery of the piece. As nearly as could be determined by the rather crude method of measurement, no grain-growth occurred unless the rod was forged below a temperature somewhere between 650° and 750°C .

(1200 and 1380° F.). Some of the results are given in Table I.

TABLE I.—*Forging Tests on Hot-rolled Rod.*

		Grain-size in mm. at edge after one hour at 700° C.	
<i>Rod diameter seven-sixteenth inch.</i>			
Original rod		0.02	
Forged cold		0.40 to 0.16	
Forged cold		0.30 to 0.18	
Forged from 900° C. to red		0.02	
Sim. Spot next to anvil		0.22 to 0.40	
Forged from 900° C. to black		0.14 to 0.22	
Forged from 900° C. to about 500° C.		0.14 to 0.40	
<i>Rod diameter nine-sixteenth inch.</i>			
Original rod		0.02	
Forged cold		0.22 to 0.40	
Forged cold		0.18	
Forged from 900° C. to red		0.02	
Forged from 900° C. to black		0.18 to 0.40	
Forged from 900° C. until cold		0.10	
Forged from 900° C. until cold		0.08	

No case of grain-growth was observed in annealed samples of hot-rolled rod, of which a considerable number were examined.

Cold-drawing.—Samples of hot-rolled rod of from quarter to half inch diameter were cold-drawn to various sizes, and samples from each draft annealed at temperatures between 650° and 900° C. (1200 to 1650° F.). No grain growth was found outside of this temperature range. In a number of tests the amount of reduction was varied by as narrow steps as possible, in some cases 0.001 in. For reasons which will be made evident, the samples in each set which were annealed at 700° C. (1290° F.) were selected for the determination of the quantitative effect of strain. Some of the results are given in Table II. From these it will be seen that, within certain limits, the grain-size after annealing is inversely proportionate to the applied strain.

On examining the samples annealed at various temperatures between the limits mentioned, it was noted that while the more heavily strained specimens showed a grain-growth after annealing within this limiting temperature range, some of these which were more lightly strained became coarsely crystalline only when annealed between about 690° and 780° C. (1275° to 1435° F.). Reheating above the latter point would refine any coarse-grained structure that might have been produced in the specimens. Photomicrographs were taken of one of these specimens as annealed at various temperatures between 675° and 780° C. (1250° and 1435° F.). A large number of specimens of this material were examined after annealing at the higher temperature, and all were found to be refined with the exception of one small section found on repolishing in which a few moderately coarse grains existed. This section was selected for photographing in order to show the narrow range of deformation within which perfect refining at this temperature probably occurs.

The analysis of this steel is: Carbon, 0.08; manganese, 0.34; sulphur, 0.032; phosphorus, 0.010; and silicon, 0.020 per cent. The reduction of area was probably about 9 per cent.

These results seem to indicate the existence of a "critical" strain affecting the annealing temperature ranges within which grain-growth occurs.

For further confirmation a number of other samples were drawn with varying reductions of area in narrow steps, and annealed at various temperatures between about 650° and 900° C. (1200° and 1650° F.). The results obtained with one series are given in Table III. and others in Table II.

Photomicrographs of this series illustrated the decrease in the grain-size with increase in the amount of deformation as found in the series annealed at 700° C. (1290° F.).

Smaller sections of the samples drawn with 8, 9, 10, and 11 per cent reduction of area and annealed at 780° C. (1435° F.) were also shown to illustrate the action of the "critical" strain. It will be noted that the samples show complete refining at this temperature until the reduction of area rises to about 10 per cent, when some coarse crystallisation still remains. With heavier reductions no refining occurs until the material is annealed at about 900° C. (1650° F.). The decrease in grain-size which accompanies increase in strain also was illustrated in photomicrographs of another series drawn with increasing reductions of area from a rod about three eighths inch in diameter.

TABLE II.—*Grain-sizes of Annealed Cold-drawn Rods.*

Diameter, In.	Diameter after drawing, In.	Reduction area, Per cent.	Grain-sizes, mm., one hour at 700° C.	Grain-size, mm., one hour at 800° and 850° C.
0.386	0.372	7	0.02	0.02
0.386	0.368	9	$\frac{1}{2}$ 0.02, 0.30 to 0.52	0.02
0.386	0.3645	11	0.27 (a few 0.02)	0.27 to 0.02
0.386	0.3595	13	0.15	0.15
0.312	0.302	7	0.52	0.02
0.312	0.296	10	0.10	0.10
0.312	0.289	15	0.06	0.06
0.312	0.280	20	0.04	0.04
0.312	0.271	25	0.036	0.036
0.384	0.336	7	0.02	0.02
0.384	0.334	8	0.50	0.02
0.384	0.332	9	0.40	0.02
0.384	0.330	10	0.22	0.22
0.351	0.342	5	0.02 (a few 0.12)	0.02 (a few 0.12)
0.351	0.339	6.5	0.02	0.02
0.351	0.338	7	0.52 to 0.72 (a few 0.02)	0.02
0.351	0.336	8	0.28 to 0.50	0.02
0.351	0.334	9	0.40	0.20 to 0.40
0.385	0.375	5	0.02	0.02
0.385	0.373	6	0.02	0.02
0.385	0.371	7	0.02 (a few 0.20)	0.02
0.445	0.429	7	0.02 (some 0.14)	0.14 to 0.02
0.372	0.361	6	0.02	0.02
0.351	0.334	9	0.50	0.02
0.351	0.324	15	0.14	0.14
0.351	0.315	20	0.05	0.05
0.351	0.304	25	0.03	0.03
0.437	0.415	10	0.20	0.20
0.437	0.404	15	0.12	0.12
0.437	0.392	20	0.04	0.04
0.437	0.379	25	0.03	0.03
0.486	0.452	7	0.02	0.02
0.486	0.445	10	0.27	0.27 to 0.02
0.486	0.432	15	0.12	0.12
0.486	0.419	20	0.05	0.05
0.439	0.416	10	0.40	0.02
0.439	0.410	15	0.17	0.17
0.439	0.392	20	0.05	0.05
0.498	0.472	10	0.22 to 0.35	0.22 to 0.35
0.498	0.460	15	0.11	0.11
0.498	0.450	20	0.05	0.05

TABLE III.—Quantitative Effect of Drawing and Annealing Rod 0.320 in. Diameter.

Diam. In.	Red area, per cent.	Grain-size in mm. after one hour at	
		700° C. (1290° F.)	800–850° C. (1470–1560° F.)
0.309	6.5	0.02	0.02
0.307	8.0	Some 0.02; rest 0.40 to 0.80	0.02
0.305	9.0	0.28 to 0.56; a few 0.02	0.02
0.303	10.0	0.25 to 0.40; a few 0.02	0.02; some 0.18
0.302	11.0	0.20 to 0.25	0.20 to 0.25
0.300	12.5	0.15	0.15
0.297	16.0	0.07	0.07

TABLE IV.—Quantitative Effect in Cold-rolling Strip Steel.

Size after cold-rolling (inch). Reduced area (per cent). Grain-size in mm. after one hour at 700–870° C. (1290–1600° F.).

Hot-rolled Strip, 0.625 in. thick.

0.059	5.6	0.034; a few 0.10
0.0575	8.0	0.03; a few 0.14 to 0.27
0.056	10.0	0.14 to 0.28
0.0545	13.0	0.09 to 0.14
0.053	15.0	0.07 to 0.11

Hot-rolled Strip, 0.064 in. thick.

0.061	4.5	0.02 to 0.03
0.0585	8.5	0.02 to 0.27
0.0575	10.0	0.21; some 0.02
0.056	12.5	0.14
0.054	15.5	0.10
0.0515	19.5	0.05 to 0.08
0.049	24.5	0.027 to 0.036

Some difficulty was encountered in duplicating the results, as the rod was frequently out of round slightly and sometimes varied locally in diameter. The greatest variations were noted in attempts to determine the lowest reduction which would cause grain-growth. Where light reductions were used the effect was frequently confined to the periphery or to local areas, the remainder of the section being unaffected. An example of this is seen in a specimen annealed at 700° C. (1290° F.). Occasionally sections were found in which the strain was unevenly distributed, as shown by the wide variation in the grain-size produced. In some lightly strained samples which apparently became refined completely at 780° C. (1435° F.), a certain "skin" effect was sometimes noted. On examining longitudinal sections of samples annealed at this temperature, a thin layer of moderately coarse grains, possibly 0.12 to 0.18 mm. in diameter, was sometimes found close to the periphery, the rest of the piece being completely refined. Allowing for these minor variations and using proper precautions, it was generally possible to reproduce these results at will. With the exception of the local effects noted, no grain-growth occurred if the reduction of area fell below about 7 per cent.

In the tabulated results some variations between the different series will be noted. These are generally due to the previously mentioned variation in the conditions of drawings.

Cold-rolled Strip.—A few samples of hot-rolled strip about 0.065 in. thick were cold-rolled with varying reductions of area. The same variation in grain-size with reduction was found with this material as with the cold-drawn steel. Refining took place only at 900° C. (1650° F.), no "critical" strain being noted. The material was too light for careful measurement, and the presence of certain irregularities in the surface made impossible an exact determination of the reduction of area. The largest grain-growth produced was much less than that obtained with the cold-drawn specimens, which had received comparatively light reduction. Some of the results obtained

were given in the previous article mentioned and are repeated in Table IV. No heavier material was available at the time the investigation was carried out, and further study was confined to a number of cases of coarse crystallisation found in strip one-tenth to one-eighth inches thick, obtained from various sources. A few cases were found in which complete refining occurred on annealing at 780° C. (1435° F.). In other cases, partial refining occurred at this temperature. In a few cases no refining occurred until the material was annealed at 900° C. (1650° F.). In the cases where complete or partial refinement occurred at 780° C., the original grain-size varied from 0.52 to 0.65 mm. in diameter. Where 900° C. was required, the grain-size was smaller than this.

(To be continued).

A REVISION OF THE ATOMIC WEIGHT OF ZINC.*

THE ELECTROLYTIC DETERMINATION OF ZINC IN ZINC BROMIDE.

By GREGORY PAUL BAXTER and MERRITT ROY GROSE.

THE success met in the electrolytic estimation of cadmium in cadmium chloride and bromide led to the hope that a similar method might be successively applied to other elements. In the case of the metallic halides it is thus possible to make a complete analysis; that is, the halogen may be determined by comparison with silver and the metal by electrolytic deposition. Where the sum of the two is essentially 100 per cent the evidence obviously is of the strongest kind that constant error has affected neither method.

The close similarity of cadmium and zinc in properties made it likely that the methods as worked out for cadmium could be applied with little variation to the determination of zinc. Such proved to be the case. We found it possible, in the first place, to deposit zinc in a mercury cathode very nearly although not quite completely, and that the zinc amalgam could be satisfactorily washed with alcohol and dried without perceptible rusting. The amalgam thus produced does not oxidise at all rapidly, even on exposure to air. The general method of procedure was essentially that described in detail in a paper upon the analysis of cadmium bromide (*Journ. Am. Chem. Soc.*, xxxviii., No. 4; *CHEM. NEWS*, xciv., p. 307). Weighed amounts of zinc bromide which had been dried by fusion were dissolved in a small amount of water in a glass electrolytic cell, and the metal was deposited as completely as possible in a mercury cathode, the bromine liberated at the anode being swept away by bubbling a slow current of hydrogen through the solution. The electrolyte was then completely freed from bromine and bromide by evaporation with nitric and sulphuric acids, and the residue was returned to the cell for further electrolysis. The amalgam finally was washed with alcohol, and dried in a vacuum, while the electrolyte was evaporated and a slight residue of zinc sulphate was weighed. In other experiments the zinc bromide was completely converted to sulphate before electrolysis.

Purification of Materials.

Reagents were purified exactly as described in the previous paper.

Zinc Bromide.—Analysis I was made with zinc bromide prepared from commercial zinc by treatment with the purest bromine and purified by many crystallisations. For the other experiments material was purified with greater care as follows: Crude metal was freed from non-metallic impurities by electrolytic transport from an anode of commercial metal through a concentrated solution of zinc bromide free from chloride to a platinum cathode,

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where the metal was deposited as a fine crystalline mass. The crystals were leached as thoroughly as possible by digesting with cold very pure water for some days, and then were dissolved by treatment with very pure bromine under dilute hydrobromic acid solution in a quartz flask. The solution was digested with an excess of zinc in order to remove more strongly electro-positive metals, and after filtration through platinum sponge was evaporated to crystallisation, and the product was three times more crystallised from very dilute hydrobromic acid solution in platinum vessels. A portion of the product was used for one analysis (Analysis 2). The remainder was fused in platinum boats in nitrogen charged with hydrobromic acid gas. The fused salt, which contained a very small amount of black material, probably carbon and silica as has been previously shown, was dissolved in water, and the solution was filtered through platinum sponge (Baxter and Hartmann, *Journ. Am. Chem. Soc.*, 1915, xxxvii., 121; Baxter and Grover, *Ibid.*, 1915, xxxvii., 1040). The solution was then evaporated to crystallisation, and the crystals were once re-crystallised from very dilute hydrobromic acid solution. In all the crystallisations centrifugal drainage in platinum Gooch crucibles was used. The final product, when fused in an atmosphere containing hydrobromic acid gas, was free from all but the merest traces of black residue.

In order to follow the purity of the product, electrodes were made from the crude zinc, from the electrolytic product, and from the four and six times crystallised salt, and the spark spectra of the electrodes were photographed with a Féry quartz spectrograph. In order to prepare electrodes from the salt, a portion was dissolved in water, and the metal was deposited as completely as possible from the solution, using platinum electrodes. The electrolytic deposit was thoroughly washed and dried, fused in an atmosphere of hydrogen in a hard glass tube, and made into electrodes by sucking the melted metal into hard glass capillaries. The crude material contained lead, cadmium, and iron. The electrolytic metal was nearly free from iron, but contained the other impurities. The four times crystallised zinc bromide contained the merest traces of cadmium and lead, while in the spectrograms obtained with the final product only the strongest lines of cadmium were barely visible. We estimate the proportion of cadmium in the final product to be less than 0.001 per cent.

To dry the salt for weighing it was first left in an exhausted desiccator over fused sodium hydroxide for some days. Then the crystals, which still contained the greater part of the water of crystallisation, were heated gently in a weighed quartz boat in a current of either nitrogen or hydrogen, charged with hydrobromic acid gas by being passed through a fuming solution of the acid gas, and dried by means of fused calcium bromide. During this process the boat was contained in a quartz tube which formed part of a "bottling apparatus." As soon as the crystal water had evaporated from the salt, the temperature was gradually raised until finally the salt was fused. After being allowed to solidify in the acid gas, the latter was replaced first with pure dry nitrogen and this in turn with pure dry air. The boat was finally transferred to the weighing bottle in which it originally had been weighed by means of the bottling apparatus.

When the weight of the salt had been determined, the boat was placed in the weighed electrolytic cell (Form II.) containing about 100 grms. of mercury, and the salt was dissolved in water in which had been used to rinse the weighing bottle (see Baxter and Hartmann, *Journ. Am. Chem. Soc.*, 1915, xxxvii., 123). Electrolysis was then begun with a current strength somewhat less than 1 ampère, and was continued for about sixteen hours. During the electrolysis a slow current of very pure hydrogen was caused to bubble through the solution in order to remove the bromine liberated at the anode. At this point the bulk of the zinc had been deposited in the mercury, and the greater part of the bromine had been

expelled. The electrolyte was now removed to a clean flask by suction, and the amalgam and cell were rinsed a few times with very pure water. The electrolyte was evaporated together with a small amount of nitric and sulphuric acids in a quartz dish. The residue of zinc sulphate, together with the excess of sulphuric acid, was dissolved in water and returned to the cell, and electrolysis was continued for some hours longer. Then the cell was again washed with chilled water which had been saturated with pure hydrogen, with especial pains not to break the electrolytic circuit until all of the electrolyte had been displaced. After the water had been removed as completely as possible the cell and the amalgam were rinsed two or three times with very pure alcohol. The cell was then stoppered, and the alcohol was evaporated in a small tubular desiccator containing fused sodium hydroxide, a Geryk oil-pump being used to exhaust the desiccator. The pressure at first was not reduced below a few mm., since the rapid evaporation of the alcohol tended to blow the stopper out of the cell, but as soon as the alcohol had disappeared the pressure was lowered as far as possible. After standing some time in this desiccator the cell and its counterpoise were placed in a second larger desiccator, also containing fused sodium hydroxide, and were left in a high vacuum for some hours before being weighed. In the meantime the electrolyte, together with the aqueous and alcoholic washings, was evaporated in the quartz dish previously used in the same experiment, and when the liquid had been reduced to a volume of a few cc. it was transferred to a weighed platinum crucible, and the evaporation continued at gradually increasing temperatures until the sulphuric acid had been expelled, and nothing but the residue of zinc sulphate remained. The crucible with its contents was then weighed.

Since in the previous work with cadmium bromide it was found that the initial weight of cadmium thus obtained is usually too large, owing probably to the formation of a small amount of mercurous bromide upon the amalgam, the electrolysis was now repeated by dissolving the zinc sulphate residue in the platinum crucible in a small amount of sulphuric acid, returning the solution to the cell and electrolysis for several hours. The process of washing was repeated in exactly the same way as before, the amalgam was dried and weighed, and the electrolyte was evaporated, and the residue of zinc sulphate again determined. In most cases a loss in weight of a few tenths of mgrm. occurred during the first electrolysis. If this was so, the process was repeated until the total weight of zinc, as obtained from the gain in weight of the cell and the zinc sulphate residue, became constant within less than a tenth of a mgrm. The results as presented in the table are computed on the basis of the final weight.

Because the process of repeated electrolysis was a laborious and time-consuming one, in several analyses the zinc bromide was converted to sulphate before electrolysis. In order to do this the boat with the fused zinc bromide was placed in a quartz dish, and the salt was dissolved in the purest water. The boat was removed with careful rinsing, the rinsings being added to the original solution. Then concentrated sulphuric acid in excess of the amount necessary to convert the bromide to sulphate was added, as well as nitric acid, and the solution was gently heated on an electric stove in order to liberate and vaporise the bromine. The temperature, however, was kept low enough so that boiling did not actually occur. After the solution had been evaporated until the volatile matter had been expelled and the zinc sulphate had separated from the residual concentrated sulphuric acid solution, the whole was dissolved in water and evaporation repeated in order to decompose bromide which might have been included in the solid residue during the first evaporation. The second residue was again dissolved in the minimum amount of water, and the solution was quantitatively transferred to the weighed electrolytic cell. Electrolysis was now carried out as usual. The amalgam was washed

and dried, and the residue of zinc sulphate in the electrolyte was determined. This residue, while never large, was always appreciable. Although in every case the zinc sulphate residue was dissolved in sulphuric acid, returned to the cell, and electrolysis repeated, the total weight of zinc obtained was never reduced by the process. The experiments in which this modification of the procedure was employed are indicated in the table. It can be seen that the results of these experiments do not differ from those in which the bromide was electrolysed directly.

The weights were standardised by the substitution method described by Richards. All weighings of the cell and of the weighing bottle containing the zinc bromide were made by substitution for counterpoises of the same material and of the same shape and size. A vacuum correction of +0.000140 gm. is applied for every gm. of zinc bromide. This is computed from the densities 4.219 for zinc bromide (Richards and Rogers, *Proc. Am. Acad.*, 1895, xxxi., 163), and 8.3 for the brass weights. A vacuum correction of +0.000003 gm is applied for each gm. of dissolved zinc. This is computed from the density of saturated zinc amalgam at 25° as found by Crenshaw, 13.343 (*Journ. Phys. Chem.*, 1910, xiv., 158). This amalgam contains 2.220 grms. of zinc in 100 grms. of mercury.

The Atomic Weight of Zinc.

Zn : Br₂. Br = 79.916.

No. of analysis.	Wt. of ZnBr ₂ in vacuum.	Wt. of Zn from amalgam in vacuum.	Wt. of residue from electrolyte.	Total wt. of Zn in vacuum	Ratio Zn : Br ₂ .	Atomic weight of zinc.
	Grms.	Grms.	Grm.	Grms.		
1.	6.88781	1.99857	0.00148	1.99917	0.408942	65.362
2.	6.79973	1.97241	0.00206	1.97324	0.408835	65.345
3.	7.67096	2.22673	0.00096	2.22712	0.409108	65.389
4.	8.02839	2.33109	0.00031	2.33122	0.409189	65.402
5.*	7.18458	2.08428	0.00219	2.08517	0.408904	65.356
6.*	7.55005	2.19143	0.00094	2.19181	0.419054	65.380
7.*	7.71332	2.23883	0.00134	2.23937	0.409096	65.387
8.	7.11551	2.06545	0.00134	2.06599	0.409146	65.395
9.	7.44099	2.16000	0.00115	2.16047	0.409140	65.393
10.*	7.18828	2.08701	0.00065	2.08727	0.409188	65.401
Average	..	..	..	..	0.409060	65.381
73.57962				21.36083	0.409063	65.381
Average, omitting Analyses 1 and 2				..	0.409103	65.388

* Changed to sulphate before electrolysis.

Since Analyses 1 and 2 were made with zinc bromide of a less degree of purity than the others, we feel that the average of Analyses 3 to 10, 65.388, represents most nearly the real outcome of the work.

Richards and Rogers (*Proc. Am. Acad.*, 1895, xxxi., 158), by comparing zinc bromide with silver and weighing the silver bromide formed, found the atomic weight of zinc to be 65.376 (Ag = 107.880; Br = 79.916). In other words, they found zinc bromide to contain 70.971 per cent of bromine, while in the present research the percentage of zinc is found to be 29.033. The sum is 100.004 per cent.

The individual results are fairly consistent among themselves, and while the agreement of the average value with that of Richards and Rogers is not absolute, it certainly affords a very satisfactory confirmation of the earlier value. Since the investigation was interrupted at this point it seems worth while to present the preliminary results. The subject is being pursued further in the T. Jefferson Coolidge, Jun., Chemical Laboratory of Harvard College.

We are greatly indebted to both the Carnegie Institution of Washington and the Elizabeth Thompson Science Fund for very generous assistance in this investigation,

ON THE RATES OF SOLUTION OF METALS IN FERRIC SALTS AND IN CHROMIC ACID.*

By R. G. VAN NAME and D. U. HILL.

FORMER papers from the Kent Chemical Laboratory of Yale University have dealt with the rates of solution of metals in iodine. (Van Name and Edgar, *Am. Journ. Sci.*, 1910, xxxix., 237; Van Name and Bosworth, *Ibid.*, 1911, xxxii., 207; Van Name and Hill, *Ibid.*, 1913, xxxvii., 543). The present investigation is an application of the same method to further measurements of the rates of solution of metals in oxidising solutions, and was undertaken on account of the probable bearing of the results upon the so-called Diffusion Theory of heterogeneous reactions.

It will be recalled that this theory is based on the hypothesis that in a reaction between two phases, let us say a solid and a liquid, the stirring of the liquid is not effective up to the actual boundary surface, but that there remains a narrow zone or layer of liquid, adjacent to the solid, which is so far unaffected by the stirring that the transport of dissolved substances through this layer, to or from the solid, must be brought about essentially by diffusion. From this point of view, the observed velocity of a reaction between a solid and a dissolved substance should be the resultant of two consecutive reactions—(a) The diffusion process, and (b) the chemical reaction proper, which occurs at the surface of the solid. (The term "chemical reaction" in this connection is used in the broader sense, and may in certain cases include processes not always classed as chemical, such as solution in water or crystallisation from solution. No such cases, however, are included in the present investigation). The slower of these two reactions will obviously determine the reaction velocity actually observed.

Many instances have come to light in recent years in which this hypothesis seems to give the best explanation of the facts. As an example, the above mentioned work on rates of solution of metals in iodine may be cited, in which it was shown that eight different metals—Ag, Hg, Cu, Ni, Co, Fe, Cd, and Zn—all dissolved at the same (equivalent) rate in a solution of iodine in potassium iodide. This fact seems to show that the rate of diffusion of the iodine is here actually the determining factor.

Such results are, of course, conditioned upon the absence of any interfering secondary effects, which are often encountered in practice and may obscure or wholly conceal the influence of diffusion. The formation of an insoluble coating on the solid is a common type of interference. Other types will be referred to later. As a rule, however, such cases show characteristic peculiarities which make it easy to determine the cause of the abnormal results. These anomalous cases can only be interpreted individually, and must, for the present, be excluded from our general discussion.

The hypothesis of a diffusion layer, together with its immediate consequences, is usually enough to account for the observed results. Nernst, however, whose opinion carries special weight since he is to a large extent the originator of the diffusion theory, has introduced a second hypothesis.

(NOTE.—Noyes and Whitney, *Zeit. Phys. Chem.*, 1897, xxiii., 689, were the first to suggest the conception of a diffusion layer, but they applied it only in a special case. Nernst, in 1904, gave the idea a more exact formulation, showed its wide applicability, and made it the basis of a "general theory of heterogeneous reactions"—see *Zeit. Phys. Chem.*, 1904, xlvii., 52; also "Theoretical Chemistry," 3rd English ed., p. 586).

Nernst argues that at the boundary surface between two phases considerable differences in chemical potential must exist between points infinitely near together, which should make the velocity of the chemical reaction infinite, or at least in practice extremely high. Consequently the diffu-

* From the *American Journal of Science* xlii., 301.

TABLE I.—Cadmium. $R'Fe(SO_4)_2$, 0.05 molar.

No. of expt.		H_2SO_4 , 0.01 molar.								K.
1.	$C = 50.00$									
	$v =$	580	560	540	520	500	480	460		
	$\Delta t =$	7	6	6	6	6	6	6		
	$c =$	0.47	2.78	4.73	6.72	8.72	10.69	12.69	14.61	
	$k_1 =$	3.96	3.93	4.04	4.11	4.06	4.18	4.04		
	$k =$	3.94	3.93	4.01	4.11	4.09	4.14	4.02		4.03
2.	$k =$	4.01	3.99	4.01	3.93	3.92	4.10	4.04		4.00
3.	$k =$	4.01	4.01	4.05	4.22	4.29	4.12	4.29		4.14
4.	$k =$	3.98	3.98	4.08	4.12	4.09	4.02	4.06		4.05
5.	$k =$	4.13	4.00	4.23	4.34	4.48	4.20	4.39		4.25
6.	$k =$	4.00	3.98	4.20	4.33	4.50	4.34	4.22		4.22
		H_2SO_4 , 0.25 molar.								
7.	$k =$	4.14	4.10	4.25	4.20	4.19	4.25	4.09		4.17
8.	$k =$	4.18	4.04	3.97	4.19	4.21	4.20	4.12		4.13
		H_2SO_4 , 1.25 molar.								
9.	$k =$	3.48	3.46	3.53	3.56	3.61	3.58	3.61		3.55
10.	$k =$	3.46	3.47	3.51	3.60	3.62	3.53	3.51		3.53
		H_3SO_4 , 5 molar.								
11.	$k =$	1.78	1.76	1.75	1.84	1.68	1.78	1.68		1.75
12.	$k =$	1.75	1.76	1.74	1.75	1.79	1.80	1.81		1.77

k_1 = velocity constant as observed, uncorrected; k = constant corrected for variations in the rate of stirring; K = average constant for the single experiment.

TABLE II.—Iron. $R'Fe(SO_4)_2$, 0.05 molar.

No. of expt.		H_2SO_4 , 0.01 molar.								K.
1.	$C = 5.00$									
	$v =$	580	560	540	520	500	480	460		
	$\Delta t =$	8	8	8	8	8	8	8		
	$c =$		4.36	8.20	11.93	15.68	19.15	22.68	25.67	
	$k_1 =$	3.90	3.93	3.90	3.99	3.78	3.59	3.73		
	$k =$	3.87	3.91	3.89	3.99	3.79	3.58	3.73		3.82
		H_2SO_4 , 0.05 molar.								
2.	$k =$	3.97	3.97	3.64	(Lost)	3.76	3.96	3.80		3.85
		H_2SO_4 , 0.25 molar.								
3.	$k =$	4.00	3.92	3.95	3.98	3.91	3.94	3.99		3.96
4.	$k =$	3.91	3.90	3.82	3.80	3.85	3.92	3.92		3.87
		H_2SO_4 , 1.25 molar.								
5.	$k =$	3.42	3.38	3.31	3.42	3.35	3.35	3.34		3.37
6.	$k =$	3.45	3.38	3.29	3.44	3.33	3.45	3.31		3.38
		H_2SO_4 , 5 molar.								
7.	$k =$	1.77	1.79	1.74	1.79	1.75	1.78	1.69		1.76
8.	$k =$	1.75	1.71	1.69	1.67	1.63	1.64	1.62		1.67
9.	$k =$	1.79	1.74	1.74	1.72	1.73	1.72	1.74		1.74
10.	$k =$	1.80	1.79	1.76	1.76	1.76	1.76	1.78		1.77

TABLE III.—Nickel. $R'Fe(SO_4)_2$, 0.05 molar.

No. of expt.		H_2SO_4 , 0.01 molar.								K.
1.	$k =$	3.75	3.75	3.53	3.29	3.27	3.33	2.98		3.41
		H_2SO_4 , 0.25 molar.								
2.	$k =$	3.82	(Lost)	3.53	3.36	3.15	3.18	3.15		3.36
3.	$k =$	3.86	3.54	3.29	3.42	3.31	3.22	3.11		3.42
		H_2SO_4 , 1.25 molar.								
4.	$k =$	3.24	3.19	3.07	2.93	2.89	2.82	2.78		2.99
		H_2SO_4 , 5 molar.								
5.	$k =$	1.71	1.69	1.56	1.52	1.49	1.45	1.45		1.55

Initial Velocities by Extrapolation.—Expt. 1, 3.80; Expt. 2, 3.75; Expt. 3, 3.75; Expt. 4, 3.27; Expt. 5, 1.71.

sion process will always be slow in comparison, and will therefore determine the observed reaction velocity in all cases, except of course the anomalous ones already mentioned.

If this hypothesis of Nernst's is to be understood literally, it means that the observed velocity of a reaction between a solid and a dissolved substance will never represent, even approximately, the true rate of the chemical reaction. No place is left for cases other than those in which the velocity is governed solely by diffusion and those rendered abnormal by disturbing influences. From this it follows that when the same dissolved substance reacts with different metals the velocity of the reaction, in all cases free from secondary disturbances, should be the same irrespective of the specific nature of the metal. This test of Nernst's hypothesis is applied in the experiments to be described.

EXPERIMENTAL PART.

The method and apparatus used have been described in a previous article (*Am. Journ. Sci.*, xxxii., 207, and in part, xxix., 237). Such minor modifications in the procedure as were found desirable in dealing with the different reactions will be mentioned in their proper connection. The different metals, in the form of circular discs 0.5 mm. in thickness and 38.3 mm. in diameter, were exposed to the action of the solution under carefully regulated conditions as to temperature, rate of stirring, and position of the disc. Samples of the solution, which was initially 600 cc. in volume, were taken at convenient intervals with a 20 cc. pipette, and the velocity constants k calculated in the ordinary way from the observed concentrations at the beginning and end of the five to ten-minute time intervals. The rate of stirring was kept at 200 revolutions per minute in all experiments, and although the variations were usually very small, they were systematically determined and corrected for by the method described in the article just cited. The temperature was 24.6° C. in all experiments with ferric salts, and 25° C. in all those with chromic acid.

Rates of Solution in Ferric Sulphate.

Previous experiments on the rate of the reaction between ferric sulphate and metals have been made by T. E. Thorpe, 1882 (*Journ. Chem. Soc.*, xli., 287), and by C. G. Schleuderberg, 1908 (*Journ. Phys. Chem.*, xii., 574). Thorpe compared the action of the ferric salt on zinc, magnesium, and iron, but under poorly defined experimental conditions, further complicated by the evolution of hydrogen. Schleuderberg studied only the reaction between ferric sulphate and copper, so that his work affords no comparison between the rates for different metals. Though primarily interested in testing for a possible effect of light on the reaction velocity, he was led to the conclusion that diffusion was the determining factor.

In the experiments of the writers, the ferric alum solutions used were approximately 0.05 molar with respect to $\text{RFe}(\text{SO}_4)_2$, and contained besides various known amounts of free sulphuric acid, together with a little ferrous sulphate to take up dissolved oxygen. Several litres of solution were prepared at one time, and the total iron concentration determined once for all by reducing duplicate samples in a Jones reductor and titrating with 0.02 normal permanganate. The ferrous iron concentration at various stages of the reaction was found by direct titration with the same permanganate solution in the presence of phosphoric acid, and the ferric iron obtained by difference. In the tables, C is the total iron and c the (variable) amount of ferrous iron contained in 20 cc. of solution, all expressed in cubic centimetres of the 0.02 normal permanganate. The values of $C - c$ were used in calculating k .

To prevent oxidation of the ferrous salt in the solution by the stirring in contact with air, an atmosphere of carbon dioxide was maintained above the liquid by passing a brisk current of the gas into the reaction vessel throughout the experiment.

In most of the experiments the ferric alum used was the

potassium salt. Those, however, in which the sulphuric acid was 5 molar were made with ammonium ferric alum, after special tests had shown that the two alums gave practically identical results.

Cadmium.—Experiments with metallic cadmium (Kahlbaum's) are recorded in Table I. Here, and in all the following tables, k_1 is the observed velocity constant uncorrected, k is the same corrected for variations in the rate of stirring, and K the averaged value of k for the single experiment. By way of illustration, data for Experiment 1 are given in full. For the rest only the corrected velocity constants are recorded.

Although it might be expected that an increase in acidity would raise the reaction velocity, it is seen in the table that precisely the reverse is true, at least for concentrations of sulphuric acid above 0.25 molar. This effect will be observed in all cases where free sulphuric acid is present, whether the oxidising agent be ferric salt or chromic acid.

Iron.—Results obtained with metallic iron are shown in Table II. The first experiment, as before, being recorded in detail as an example. The calculation of the constants from the titrations is here somewhat different, since for every two molecules of ferrous iron formed by reduction of the ferric sulphate one more is formed by solution of the metal. The concentration of ferric salt at any instant is therefore measured by the value of the expression $C - c_0 - \frac{2}{3}(c - c_0)$; in which C is the total iron, c_0 the initial ferrous iron, and c the ferrous iron at time t , all expressed in the same units. In the table these units, as before, are cubic centimetres of 0.02 normal permanganate, and the values refer to 20 cc. of solution. The metal used was "American ingot iron," a special grade of commercial iron which has a purity of about 99.9 per cent.

For the lower acidities, 0.01 and 0.05 molar, the results are less trustworthy than the rest and probably slightly too low, for the disc became covered during the experiment with a blackish coating which seemed to consist chiefly of hydroxide, since it turned to a rust-red colour on drying. In the presence of 0.25 molar sulphuric acid the coating was very slight, and at higher acidities entirely absent.

Nickel.—Table III. contains the results of the experiments with metallic nickel. Two samples of "pure nickel" were used—one furnished by Kahlbaum the other of unknown origin—both of which seemed to give practically the same results. The former was used in Experiments 1 and 2, the latter in Nos. 3, 4, and 5, and also in the experiments with chromic acid to be described later.

In no case was the action of the solution on the metal perfectly normal and uniform. In the presence of 0.01 and 0.25 molar sulphuric acid distinct black coatings formed on the disc; while even at the highest acidity, 5 molar, the disc acquired a brownish discoloration and, ultimately, a minutely spotted appearance. Examined under low magnification these spots were seen to consist of irregular rounded hollows, each containing traces of a brown deposit.

As the probable result of these irregularities in the action, we find in all cases that the velocity constants decrease as the experiment progresses, though less rapidly in the more strongly acid solutions. However, the constants for each single experiment, when plotted with time as the other co-ordinate, lie fairly close to a straight line, so that by extrapolating this line back to time zero we obtain a corrected value for the reaction velocity which represents, at least approximately, the rate at which the reaction would proceed under the given conditions if the sources of disturbance were absent. The initial reaction velocity for each experiment, as obtained by such extrapolation, is recorded at the foot of the table. Although, owing to irregularity in the constants, this procedure sometimes fails to give sharp results, these extrapolated values are certainly more accurately and fairly representative of the single experiments, in the present case, than are the average values of their constants, and will therefore be given the preference in comparing nickel with the other metals.

It should be noted that this process of extrapolation affords a general method for correcting the observed reaction velocities for the effect of all disturbances which are initially absent but are produced by the progress of the reaction. It will be used in a number of the cases to follow.

(To be continued).

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Ordinary Meeting, November 24, 1916.

Prof. C. V. BOYS, F.R.S., President, in the Chair.

A PAPER "On the Measurement of the Thomson Effect in Wires" was read by Mr. H. R. NETTLETON.

The paper describes how absolute measurements of the Thomson effect may be made in wires. The theory is fully worked out, and the sources of error likely to arise—especially owing to the smallness of the area of cross-section—are considered. The method is sensitive, consistent, and very rapid; its ultimate object is to determine the Thomson effect at different temperatures in a number of metals, both rare and base, at the same time, and with the same specimens, finding their thermo-electric powers. The preliminary experiments of this paper, testing the method, are with constantan wires of different lengths, with manganin, and with German silver.

DISCUSSION.

* Mr. F. E. SMITH suggested that the method might have been modified by having two exactly similar systems arranged in opposite arms of a Wheatstone bridge, so that the current passed from hot to cold in one wire and from cold to hot in the other. Any change in the relative temperatures of the two wires on reversing the current would be indicated by the bridge being thrown out of balance. This seemed preferable to measuring the temperature of a wire by the resistance of another wire wound round it.

Mr. D. OWEN thought the method was very satisfactory. Had the author thought of using electrical heating for the hot end in order to get smaller temperature gradients, in view of the high sensibility of the arrangement? He thought the figures of Oosterhuis stood in need of verification. If the author could adapt his method to deal with crystals, such as were employed in wireless detectors, the results would be of very great interest.

Dr. R. S. WILLOWS said that it was difficult to see from the equations which Mr. Nettleton had put down on the board whence the energy was derived in cases such as those mentioned in the paper which Mr. Darling was about to read. In some of these cases dE/dT and d^2E/dT^2 were both zero. It would be useful if the method could be rendered applicable to substances with large temperature coefficients.

Prof. W. ECCLES said he had hoped that the author would have explained just what the important points of the method were in a less abstract manner—with the aid, say, of diagrams of the temperature conditions along the wire before and after the current reversal.

The AUTHOR, in a written reply, thanks Mr. F. E. Smith for his suggestion, which, however, as regards sensibility, would depend on the value of the temperature coefficient of resistance, and might carry with it additional complications such as those which enter into King's experiments. In reply to Mr. Owen, the use of electrical heaters would simplify temperature coefficient work enormously, but unfortunately there are mechanical difficulties arising out of the facts that the solder fixing the wire must be applied from behind, and that, in order that the resistance of the wire may be measured as a low resistance *in situ*, the copper must be narrowed down, as shown at K in Fig. 2, leaving a very small bearing surface at N. The author

still hopes that he may be able to overcome these difficulties, while ensuring at the same time that the difference of temperature U , measured by the thermo-couple, is substantially that between the extremities of the wire. He agrees with Mr. Owen that the results of Oosterhuis should be confirmed, as well as those of Alderink, in view of the extraordinary conclusions to which they lead; at the same time, he has a very high opinion of the methods adopted at Groningen, and his own results on mercury some time ago were not very different from those of Schoute. In reply to Prof. Eccles, the author has himself felt the difficulty of explaining the essence of the method simply and satisfactorily. Graphs of the distribution of temperature afford little help. What is actually done is explained in a few words in Section 2 of the paper, though no simple proof of the formula is given. A "proof" of the formula $\sigma = R(C_2 - C_1)/SU$ is obtained very simply by equating the electrical heat produced per second per centimetre—viz., $C_1^2 R/SL + C_1 \sigma U/L$, when C_1 is passing from hot to cold, to that produced when C_2 is passing in the opposite direction—viz., $C_2^2 R/SL - C_2 \sigma U/L$. This proof was omitted not so much because it assumes that σ , R , and the temperature gradient are constant everywhere, and ignores emissivity, as because it neglects thermal conductivity, or assumes that Joulean and Thomson heat are propagated similarly. In reply to Dr. Willows, the method is equally applicable to wires of large temperature coefficient. Equation (2B) may then be applied, or Equation (2C) if the resistance of the wire be measured directly while under temperature gradient, as suggested in Section 4D. The author has no satisfactory explanation of the energy problems arising out of the researches in Holland or those arising from Mr. Darling's experiments; in the absence of measurements of σ and π there are few data to go upon. In the case of Mr. Darling's experiments, it must be remembered that though with, say, the bismuth silver couple over the range $300^\circ\text{C}.$ — $500^\circ\text{C}.$, both dE/dt and d^2E/dT^2 are zero, no additional energy or thermo-electric force is manifest. If the law of successive temperature is true with Mr. Darling's materials, a thermocouple composed of molten bismuth and silver with one junction at $300^\circ\text{C}.$ and the other at $400^\circ\text{C}.$ or $500^\circ\text{C}.$, should show no E.M.F. corresponding to zero Peltier effects and equality of Thomson coefficients.

A paper "On the Thermo-electric Properties of Fused Metals," by C. R. DARLING, A.R.C.S., F.I.C., and A. W. GRACE, was read by the former.

One of the authors has for some time been investigating the possibility of using base metal thermo-couples at temperatures above the melting-point of one of the constituents. For this purpose it was necessary to determine whether any peculiarities in the thermo-electric behaviour of metals occur at fusion. In the case of lead, tin, zinc, and cadmium there is no perceptible break in the continuity of the curves obtained. In couples containing bismuth, however, several cases were noted in which the E.M.F. remained constant for a wide range of temperature after the fusion of the bismuth. This occurs with silver, aluminium, iron, or nichrom as the other element. Useful applications of this property are discussed. No attempt was made to construct a thermo-electric diagram from the results, as it would be impossible to obtain correct values of dE/dt at all parts of the curves, many of which show small flexures, without making more accurate measurements in the region of such flexures than was practicable.

DISCUSSION.

Mr. A. CAMPBELL, in a communication which was read by the Secretary, remarked that he had made similar experiments (*Proc. Roy. Soc. Edin.*, 1888) on Wood's metal, an alloy of bismuth melting at $73^\circ\text{C}.$ The results of measurements against iron from $8^\circ\text{C}.$ to $150^\circ\text{C}.$, when reduced to a thermo-electric diagram, gave one straight line up to the melting-point, and another straight line, of a different slope, above the melting-point. He disagreed

entirely with the authors' remarks on the usual thermo-electric diagram. A diagram of the thermo-electric powers was most valuable, even though the lines may not be straight at the extreme temperatures. If anything is to be deduced from observed results, the first step is to plot the thermo-electric powers against temperature. Why the authors give results of tests against a whole series of metals is not clear. A set of tests against one metal would have been sufficient to fix the bismuth curve on the thermo-electric diagram, and all the other results could then have been deduced from the curves of the other metals already determined by more exact methods.

The PRESIDENT expressed himself puzzled by the results shown in Fig. 2. Up to the melting-point of bismuth the different metals gave with it increasing E.M.F.'s. At the melting-point, however, discontinuities occurred, and it appeared that if one eliminated bismuth by subtracting the ordinates of one curve from another, discontinuities would also occur, at the melting-point of bismuth, in the properties of the couples obtained by combining the other metals *inter alia*. This, of course, was not true.

Prof. HOWE pointed out that there was not a marked discontinuity in the difference of the nickel and copper curves when this was plotted. The President's remarks held, however, in the case of silver with either of the others.

Mr. S. W. SMITH pointed out that bismuth was abnormal in that it contracts on melting.

Dr. R. S. WILLOWS mentioned that the metals lead, tin, zinc, and cadmium, which had been shown to have no thermo-electric discontinuities at their melting-points, happened to be those which, as Mathiessen had found, formed alloys with one another of which the specific resistance could be deduced from the percentage composition. He suggested that the discrepancy mentioned in the case of iron might possibly be due to the occurrence of some allotropic modification, in which case there was really a change in the substance, and it was unfair to extrapolate the thermo-electric diagram beyond the change point.

Mr. DARLING, in reply, said he had no doubt that Mr. Campbell's remarks would hold if one could get out the proper thermo-electric diagram. Owing to the numerous little kinks which occur, very sensitive temperature measurements are required. If really accurate diagrams could be obtained it might then be possible to deduce the properties of any bismuth couple from those of one, as Mr. Campbell suggested. They had tried this in a few cases, however, but did not get good agreement. He did not know whether the peculiarity of bismuth which had been mentioned was related to the phenomena which they had described. Bismuth was a freak metal in many respects. He was unable at the moment to solve the difficulty raised by the President. Their aim had been, primarily, a practical one, and they had not gone as fully into points of that nature as might have been desired.

SOCIETY OF GLASS TECHNOLOGY.

THE second meeting of the Society was held on December 14, 1916, in the University of Sheffield, the President (W. F. J. WOOD, B.Sc.) taking the Chair.

Dr. H. FRANK HEATH, C.B., of the Advisory Committee of the Privy Council, addressed the meeting, pointing out the good services the Society could render to the nation, and assuring it of the Government's interest and support.

The remarkable developments that have taken place in the glass industry during the last two years were emphasised by an exhibition of various types of glass including (a) Scientific Ware, (b) Optical Glass, (c) Artistic Glass, (d) Miscellaneous Exhibits. Many firms and private individuals sent collections for exhibition, and it was apparent that in chemical ware and other

scientific glass, there was no necessity to depend on German production in the future. Beautiful specimens of artistic glass, both ancient and modern, were shown, whilst there were several interesting and instructive exhibits of glasses illustrating various phenomena met with in glass production.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxliii., No. 16, October 16, 1916.

Chemical Action of Sodium Peroxide on Oxides of Carbon.—C. Zenghelis and Stavros Horsch.—Sodium peroxide reacts energetically with carbon monoxide; a slight rise of temperature occurs and carbonate is formed. With the dioxide the action is more intense and the rise of temperature greater; active free oxygen is evolved. The heat of the second reaction is less than that of the first, and the authors suggest that the second reaction takes place in two stages. In the first phase two CO_2 molecules add themselves on to one molecule of Na_2O_2 to give the percarbonate $\text{Na}_2\text{C}_2\text{O}_6$, which is then decomposed in the second phase. When sodium peroxide is mixed with any oxidisable substance, such as aluminium, and carbon dioxide is passed over the mixture a violent reaction occurs often ending in an explosion. The action of the CO_2 raises the temperature to that of combustion of the substance present, and each molecule of CO_2 sets free a molecule of active oxygen. Thus the reaction occurs spontaneously. If magnesium is substituted for aluminium a violent explosion occurs; iron burns without an explosion, the product fuses and finally if a little powdered iron is added Na_2FeO_4 is formed. Zinc and copper both burn if the mixture is heated strongly.

Action of Sulphur upon Baryta in Presence of Water.—L. Guiteau.—When a mixture of two parts of hydrated baryta, one of sulphur, and 25 of water is boiled a liquid is obtained which is nearly black when hot, becoming orange-red on cooling. The solution when allowed to stand decomposes slowly, giving hydrated hyposulphite of barium, and sulphur, with liberation of sulphuretted hydrogen. But if it is evaporated by heating, red prisms of barium tetrasulphide ($\text{BaS}_4\cdot\text{H}_2\text{O}$) mixed with sulphur and hyposulphite are obtained, while the orange mother-liquor appears to contain the persulphide BaS_5 . This compound is unstable and readily decomposes as follows:— $3\text{BaS}_5 + 3\text{H}_2\text{O} = \text{BaS}_4 + \text{S}_2\text{O}_3\text{Ba} + 3\text{H}_2\text{S} + \text{S}$.

Crystalline Liquids obtained by Evaporating a Solution.—P. Gaubert.—When a solution of anisal-*p*-amidoazotoluol in ether, benzene, &c., is evaporated on a piece of glass a birefringent liquid phase is produced, which is green by reflection. The green colour is due to the existence of very unstable liquid crystals, which are optically negative. When the liquid solidifies it gives rise to two unstable forms differing from that obtained from the anisotropic liquid produced by fusion. The author has similarly studied liquid crystals from ethyl anisalaminocinnamate, *p*-azooxyanisol, esters of cholesterol, and active amyl cyanbenzal aminocinnamate.

MEETINGS FOR THE WEEK.

TUESDAY, 9th.—Royal Institution, 3. (Christmas Lectures, adapted to a juvenile auditory). "The Human Machine which all must Work," by Prof. Arthur Keith, M.D., F.R.S., &c.

THE CHEMICAL NEWS

VOL. CXV., No. 2981.

SYNTHETIC CHEMISTRY AND THE RENASCENCE OF BRITISH CHEMICAL INDUSTRY.*

By Prof. GILBERT T. MORGAN, F.R.S.

(Concluded from p. 3).

IN 1863 Béchard discovered the first aromatic arsenical, a substance produced by the interaction of aniline and arsenic acid. He described this compound and a few of its salts, but came to an erroneous conclusion in regard to its constitution. For thirty-nine years this imperfectly-described product remained one of the unconsidered trifles of synthetic chemistry hidden in an out of the way corner of Beilstein's "Handbook." Then it was found to be of value in the treatment of sleeping sickness, and received the name of atoxyl. Its true constitution was unravelled in 1907 by Ehrlich and Berthelm, and, in the hands of the former worker, atoxyl became increasingly valuable as the parent substance of the very important drug, salvarsan. In his epoch-making researches Ehrlich has emphasised the necessity for preparing new compounds by giving to salvarsan its numerical synonym of 606. Before obtaining the optimum therapeutic effect he had had to prepare and examine 605 organic arsenicals, many of these being new compounds specially synthesised for the end in view. Could Ehrlich have shortened his task by an application of the phase rule or some other mathematical device, he would certainly have done so, but the toilsome empirical method was the only way.

The processes of synthetic chemistry although laborious are quite in accordance with Nature's mode of progression. When she wishes to make an oak she produces sufficient acorns to stock a forest. In synthetic chemistry as in the struggle for existence among living organisms "Many are called, but few are chosen."

The gift for synthetic chemistry is a type of genius best defined in Edison's terms as "1 per cent inspiration and 99 per cent perspiration."

Although many of the greatest triumphs of synthetic chemistry have been won by German workers it is not wholly because German chemists are more gifted in this respect than the chemists of other lands. The proof of the chemical constitution of the colouring principles brazilin and hæmatoxylin by W. H. Perkin, jun., and his co-workers and a recent memoir by the former on the rare alkaloids cryptopine and protopine, show what English chemists can do when they turn their minds and energies to synthetic chemistry.

Synthetic indiarubber was first produced by Sir William Tilden, the founder of this society, and many of the later developments in rubber research have been worked out by English chemists.

The trouble with us is that as a nation we have no faith in the utility of synthetic chemistry, and our chemists do not receive the financial support which alone can render their work fruitful on an extensive scale.

One large German chemical firm is reputed to have set aside one million pounds sterling to capture synthetic rubber. We have often heard of the other large German organisation which expended £1,000,000 in accomplishing the commercial synthesis of indigo.

It is of interest to note that even in this success there is no finality for this particular synthesis—from naphthaline—is in course of becoming superseded by another German

synthesis, in which benzene is the starting point. The latter is the process employed at the Port Ellesmere Works, which have now been acquired by Messrs. Levinstein, Ltd., of Manchester.

The working of this indigo process on a commercial scale will lead to the production of large quantities of chloroacetic acid and sodamide, which will be available for other synthetic operations besides the making of indigo. The synthetic chemist or molecule juggler—as he has been recently designated—has long had an affection for sodamide, this substance being a marvellous weapon of synthetic research, both in inorganic and organic chemistry. Treated with nitrous oxide it yields sodium azide, from which many other azides, both inorganic and organic, have been prepared. Certain of the latter were first made in this college by Dr. Forster and his assistants. Most of these compounds are powerful explosives, but in this country they have been regarded merely as freak chemicals and laboratory curiosities. Long before the war the German War Office had studied these azides, and one of their service detonators is the violent explosive, lead azide.

The azides subserve more peaceful projects; they interact quantitatively with diazonium salts yielding organic azides convertible into aminophenols and aminonaphthols. These aminohydroxy derivatives furnish dyes having the valuable property of forming black lakes with chromium and copper compounds.

Cheap sodium azide will lead to useful developments in colour chemistry. Sodamide itself interacts with a great variety of aromatic substances. With β -naphthol it furnishes 5-amino- β -naphthol, a product recently suggested as a component of certain ingrain dyes. Tschischibabin, a talented Russian chemist, has been able in spite of the distractions of war to study the condensation of sodamide with the base pyridine obtainable both from coal-tar and bone oil. The products are 2-aminopyridine and 2:6-diaminopyridine, which furnish a variety of interesting products showing promise of becoming useful in colour-making.

These illustrations are employed to indicate that synthetic chemistry is not restricted to the study of organic compounds. The possibilities of inorganic synthesis are boundless, and each advance in this field of synthetic chemistry accelerates the rate of progress on the organic side. Moreover, there is a vast domain still very largely to be explored where these two branches of chemistry—the inorganic and organic—mingle and blend together. The organo-arsenical drugs—to which I have already referred—are first fruits of the harvest to be garnered in this fertile field of research. Sodium hydrosulphite, discovered by Schützenberger, remained for a long time a laboratory curiosity seldom isolated in a solid condition. The gradual development of the indigo problem led to greater and greater demands for this salt, which was finally put on the market in a solid form by the Badische firm. Formaldehyde, which was first manufactured on a commercial scale about thirty-five to forty years ago, has since been employed in a great variety of organic syntheses, many of considerable importance. When condensed with sodium hydrosulphite, formaldehyde furnishes sodium formaldehyde sulphonylate—a valuable reducing agent—sold under the name of rongalite. This aldehyde condenses readily with the aromatic bases, aniline and its homologues and derivatives, and one of the earliest industrial successes was the use of formaldehyde in furnishing the central methane carbon atom in rosaniline and other triphenylmethane dyes. Formaldehyde condenses with aniline, yielding diaminodiphenylmethane, and this diamine oxidised with a third molecule of aniline in presence of aniline hydrochloride furnishes pararoaniline hydrochloride or paramagenta. The same processes applied to *o*-toluidine gave new magenta, discovered in 1889. Since then many other colours have been made through the intermediary of formaldehyde, notably in the di- and triphenylmethane series and in the acridine group.

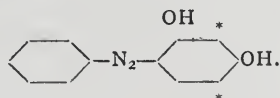
* The Inaugural Address to the Royal College of Science Chemical Society for the Session 1916-17.

Formaldehyde condenses energetically with the phenols, and in the hands of Baekeland, a Belgian chemist, working in America, this reaction has given rise to the artificial amber—*bakelite*. Condensation of formaldehyde with phenol- and cresol-sulphonic acids led to valuable tanning materials invented by Stiasny and exploited by the Badische firm, despite the fact that the discoverer was working in England.

A former member of this society, Dr. G. H. A. Clowes, working in collaboration with Prof. Tollens, of Göttingen, found that formaldehyde and many of its derivatives, $\text{CH}_2(\text{OX})_2$ and $\text{CH}_2(\text{NH}_Y)_2$, reacted quantitatively with phloroglucinol to give an insoluble red condensation product $(\text{C}_7\text{H}_6\text{O}_3)_x$, which could be used in the estimation of formaldehyde and of labile methylene groups. This principle has been utilised industrially in the fixation of azo-dyes derived from resorcinol, *m*-aminophenol and *m*-phenylenediamine.

These colouring matters are first dyed on woollen fabrics in the ordinary way from an acid bath and then fixed by treatment with formaldehyde.

The simplest example of a dye suitable for this process is:—



The formaldehyde attacks the dye at the marked positions, adding on methylene groups and yielding sparingly soluble condensation products.

The Vulcan dyes of Messrs. Levinstein are a series of colouring matters which can be thus fixed by the formaldehyde after treatment. In printing, the formalin solution is replaced by solid hexamethylene-tetramine, which, in the process, liberates methylene groups.

The mention of hexamethylene-tetramine reminds one of another use of formaldehyde—namely, in the synthesis of drugs. Hexamethylene-tetramine itself is one of the newcomers in the last edition of the "British Pharmacopœia."

The significance of the indigo synthesis lies in the circumstance that it can be used not only in the production of the naturally occurring blue dye, indigotin, but also in the manufacture of other colouring matters not found in nature.

The oxidation of indoxyl—an intermediate stage in the indigo-synthesis—leads to isatin, and at present much activity is being manifested in the manufacture of mixed indigoid dyes from this compound. Thioindigo scarlet is a successful cotton dye produced by condensing isatin with oxythionaphthene (Kalle, 1910).

These indigoid pigments form a section of the important class of vat dyes which are nowadays reduced to their alkali-soluble leuco-derivatives with alkaline sodium hydro-sulphite to form the so-called "vat" in which the textile fabrics are dipped and subsequently coloured by exposure to the atmosphere.

The early years of the twentieth century saw the discovery of the important vat dyes of the indanthrene series, the earliest members being described by R. Bohn in 1901. Until the outbreak of war these indanthrene dyes were entirely a German monopoly, and one of the first endeavours of dye makers in this country has been to work out processes for the production on a manufacturing scale of indanthrene blue and its allies. A German colour chemist predicted that no British firm could produce the colours within ten years of the commencement of war; but recently British Dyes Limited have put on the market a blue of this type called chloranthrene blue, a very creditable step in advance considering that the only guidance available were the German patent specifications. Another British firm, Messrs. T. Morton, of Carlisle, were even earlier in the field with an indanthrene blue, which they claim to have produced for their own use in February, 1915.

One remarkable feature of synthetic chemistry in recent years has been the hydrogenation of divers organic compounds in the presence of catalysts. The hardening of vegetable and fish oils by hydrogen in presence of palladium or finely-divided nickel is an important instance of this process.

Quite recently, Brochet, a French chemist, has shown (1915) that the vat dyes are amenable to this treatment. Indigotin is readily reduced to indigo-white by hydrogen in the presence of finely-divided nickel and caustic soda. The indigo-white solution thus prepared is free from excess of reducing agent. Other vat dyes may be reduced in a similar manner, so that the reaction will tend to extend the dyeing of vat colours to fabrics in which excess of alkaline reducing agent is detrimental.

The ordinary commercial method of manufacturing aniline, toluidine, or α -naphthylamine is by reducing the corresponding nitro-compound, nitrobenzene, nitrotoluene, or α -nitronaphthalene with iron borings and water slightly acidified. The yields are so good and the reagents so cheap that it would at first sight seem unlikely that the process could be displaced by any other method of reduction. But synthetic chemistry knows no finality, and progress gained in one direction leads to pioneering experiments along other lines. Strenuous efforts are being made by two large German firms, the Badische Company and the Höchst Works, to bring about economically the direct reduction of nitrobenzene and other nitro-compounds with hydrogen in the presence of catalysts.

Already it is claimed that when nitrobenzene distilled in steam is passed together with hydrogen over finely-divided nickel heated at 120° , an almost theoretical yield of aniline is obtained. Many variants of this experiment are being tried with all kinds of catalytic agents, and it can scarcely be doubted that these efforts will ultimately be crowned with success.

All these things, and more, are possible in a land where belief in synthetic chemistry forms a part of the national creed.

These reflections lead me to deal briefly with the personal aspect of the subject.

Synthetic Chemistry as a Life Work.

In considering such a problem as synthetic chemistry from the social standpoint it must not be forgotten that the chemists who are to undertake this work are generally men and women who need to earn a livelihood in this pursuit. Accordingly they must receive sufficient remuneration to find them food, clothing, and shelter, and since "man does not live by bread alone" their profession should also ensure them the goodwill and esteem of their neighbours and fellow countrymen.

It is at this point that we chiefly fail. We have the fertile brains and the trained fingers for synthetic chemistry, but it has not hitherto paid the young chemist to make the pursuit of synthetic possibilities his life work. The pushful commercial traveller making a good income by selling foreign dyes on a commission basis is much more highly esteemed among us than the plodding chemist working patiently year in year out on the off-chance of hitting on a paying product. For although I have referred to a few of the commercial successes of synthetic chemistry I have not mentioned the industrial failures, yet their name is legion and they are enshrined in the dozen bulky volumes of Friedländer's "Fortschritte," yet the work which leads to the production of these industrially unimportant compounds is just as good and just as patiently performed as that which very occasionally achieves a commercial success. The search for a useful dye or drug is greatly like the proverbial "looking for a needle in a haystack." In Germany they are kinder than we are to the synthetic chemist who has not found the needle, and he in return is animated by a high sense of duty and loyalty.

We are brought face to face with singularly conflicting traits in the British character. The men who find it

intolerable to submerge their individuality sufficiently to spend their working years in a chemical factory will, nevertheless, bravely fling away their lives in a few days, sometimes even in a few hours, on the battlefields of Flanders. That these sacrifices are made on the score of patriotism goes without saying, but they are made the more willingly and gaily because they appeal to the sporting instincts of the British races.

What can be done to impart this appeal to the sporting instincts into our chemical industries? It will have to be done if we are to recover long lost ground. The collegiate spirit needs to be introduced into chemical factories and industrial laboratories, so that individuals may feel that the success for which they are striving is the credit of the team and not necessarily that of its individual members. This ideal can be attained only if the team is captained by leaders who can inspire loyalty, and who will take care that not only those who gain the few prizes but also those who try consistently receive their due reward.

Already in a few of our factories an earnest attempt has been made at inculcating a feeling of corporate life. It is a problem which bristles with difficulties, for although the usual error is to leave the matter entirely alone, on the other hand the incorporation may easily be overdone.

It is a satisfactory feature of the times that young chemists entering on an industrial career are welcomed by their employers to an extent that was never noticeable before the war. They begin at higher salaries, they are treated with greater respect, and are offered better prospects than was the case before our eyes were opened to the parlous condition of our great industries.

At a critical point in the first French Revolution, when matters seemed to have reached a deadlock, Barbaroux, a deputy from Marseilles, sent home a spartan message for 600 men who knew how to die. Six hundred Marseillaise responded, and as they trailed their pikes along the dusty road to Paris they sang the Marseillaise, the immortal hymn of liberty.

The circumstances of the British Empire are as desperate to-day as were those of the youthful French Republic in 1792. The credentials of our sovereignty are being weighed in the balance, not only by our enemies but also by our allied friends and neutral acquaintances. Our chemical industries, the basis of our supply of war munitions, are in pressing need of trained chemical workers. In this extremity one may not inappropriately paraphrase Barbaroux, and call for 600 young chemists who know how to synthesise.

GRAIN-GROWTH IN DEFORMED AND ANNEALED LOW CARBON STEEL.*

By RALPH H. SHERRY, M.A.

(Concluded from p. 6).

Cold Pressings.—The quantitative study of grain-growth in low-carbon steel pressings is decidedly difficult if the action of the strain is at all complicated. In certain cases the amount of strain can be determined relatively, as, for instance, in operations such as bending, light drawing, and forming. In a drawing operation, which was illustrated, representing a blank and a pressing to be formed, if the operation is carried out with no reduction in the thickness of the metal, the amount of strain can be determined relatively.

An outer circle represents the circumference of the blank, an inner circle the circumference of the pressing. In the pressing operation the periphery of the blank becomes the top of the pressing and receives the heaviest strain. The bottom of the pressing receives little or no strain. In the side walls are zones in which the strain increases regularly from the bottom to the top. These zones are included

in the area between the inner and outer circles. The strains existing in these zones can be represented relatively by the frustrum of a cone of the same height as the pressing, the radii of the upper and lower bases being respectively equal to the radius of the blank and the radius of the pressing. In such a figure the radius of the smaller base represents the zero point of measurement. The difference between the radius of the smaller base and the radius of the larger base represents the maximum amount of strain received by the pressing.

A diagrammatic representation of the relative strains in a typical pressing operation was given.

If a pressing of this type is annealed at 700° C. (1290° F.) and examined, it will be found that there has been considerable grain-growth, large at the bottom, and decreasing in size regularly toward the top.

Strips were cut from a number of such pressings and annealed at various temperatures between 600° and 900° C. (1110–1650° F.). On examining samples annealed between 690° and 900° C. (1275° and 1435° F.) it was noted that a sharply defined zone of marked grain-growth occurred near the bottom of the pressing. Near the top of the pressing a zone was found in which the grain-size was normal. In the central zone extending between the bottom and top zones the grain-size decreased gradually until it became normal. No grain-growth occurred at the bottom. On reheating to 790° C. (1450° F.) partial refinement took place in the lower zone. Samples annealed between 780° and 875° C. (1435° and 1605° F.) showed rather moderate grain-growth in the lower zone, decidedly less than that obtained on annealing between 690° and 780° C. On annealing below 650° C. (1200° F.) for periods of time up to six hours, no grain-growth was found. On annealing between 650° and 690° C. no grain-growth occurred in the lower zone and only a moderate growth in the central zone. Photomicrographs illustrating the effect of the various annealing temperatures were shown. In preparation for these, parallel strips were cut through the pressing and annealed at the temperatures noted. The photomicrographs represent the same relative position in the pressing. No variation for increase in size was noted.

A similar condition was noted on experimenting with a number of pressings of widely varying gauge, which had received moderate drawing, bending, or forming. These results tend to confirm the existence of the "critical" strain noted in the experiments with the cold-drawn steel. That refining occurs at about 780° C. (1435° F.) was noted in actual practice with many pressings in which the presence of coarse grains had prevented further operations. After annealing at about 790° C. (1450° F.) the metal could be readily worked. In a comparative small number of cases where the operation to be performed was somewhat severe it was necessary to anneal at 900° C. (1650° F.).

Effect of Carbon.

The observations of nearly all the investigators of the subject tend to show that grain-growth to any appreciable extent will not occur in steel that has a carbon content uniformly above 0.15 to 0.18 per cent. While no exact determination was made, this was practically confirmed in this investigation. Grain-growth was observed in certain cases in steels of from 0.18 to 0.20 per cent carbon, but only in the ferrite bands present. A photomicrograph of a case of this kind was shown. Where no ferrite bands were present and the steel was uniformly 0.18 per cent or higher in carbon content, no appreciable grain-growth was observed. The results of microscopical examination were confirmed by the results obtained in commercial practice. In several cases where coarse crystallisation proved to be a serious factor in the manufacture of pressings of low-carbon steel, the difficulty was eliminated by the use of steel containing about 0.20 per cent of carbon.

A study was made of some pressings from seven-sixteenth inch plate which was slightly decarbonised on the surface.

* A Paper read before the Faraday Society, December 18, 1916.

Two varieties of steel were examined, one a 0.20 per cent. carbon steel of ordinary basic open-hearth analysis, and the other a chrome-nickel steel of the following analysis:—

Carbon	0.17 per cent.
Manganese	0.60 „
Sulphur.. .. .	0.038 „
Phosphorus	0.018 „
Nickel	1.0 „
Chromium	0.42 „

After the pressing operation, which consisted in forming from the blank a cup-shaped pressing about 2½ in. high and 3 in. in diameter, with a slightly flanged top, strips were cut from the top to the bottom and annealed for one hour at 715° C. (1300° F.). Photomicrographs of a set of these strips were shown.

The effect of increasing carbon content is quite strikingly shown in these specimens. In the decarbonised layer the grain-growth, while not exceedingly large, is very marked and appears to some degree in the ferrite bands. In narrow ferrite bands grain-growth to any appreciable degree appears to be checked between the pearlite walls and is frequently shown only by the elongation of the grains between the walls. Wherever the pearlite is present in sufficient quantity to surround the grains, no appreciable grain-growth seems to occur. In the wider ferrite bands there is usually more appreciable growth.

There are a number of factors which make the study of the effect of carbon by the use of decarbonised steels rather difficult, and, to eliminate as many of these as possible, some other method of procedure becomes necessary. It should be possible to obtain excellent results by preparing a series of steels of varying carbon content in the form of hot-rolled rod, drawing each individual rod with varying reductions of area. Because of the greater possibility of control of the variable factors, this method would permit of a more accurate study of the effect of carbon.

Examination of the chrome-nickel steel pressing, which was only slightly decarbonised, showed that while grain-growth occurred, it was of less extent than in the carbon-steel pressing. The pressings were alike, being made with the same die and punch. Grain-growth was generally of greater extent in the ferrite bands than in the surrounding areas, and the growth in some of the larger ferrite bands was practically of the same extent as in the surface layer. The same suppression of growth in the presence of pearlite was noted, although not quite so marked, possibly owing to the lower carbon content.

Analysis of the Steels.—The carbon content of the various carbon steels examined during this investigation varied from 0.05 to 0.18 per cent. All were basic open-hearth stock, with the usual content of other constituents.

Physical Properties.

While the most noticeable difference in the physical properties of normal and coarse-grained low-carbon steel is in resistance to shock, some marked differences were noted in the tensile properties. While these may vary in sheet according to the conditions of rolling, the presence of coarse grains usually caused a lowering in the elastic limit and in the elongation. Some instances are given in Table V. Under normal conditions the physical properties of hot-rolled sheet were found to be as follows:—Elastic limit, 30,000 to 35,000 lb. per square inch; maximum strength, 45,000 to 50,000 lb. per square inch; elongation in 2 in., 42 to 52 per cent.

Duplicate samples from the same sheet usually gave similar results. After annealing at 900° C. (1650° F.), the tensile properties became quite normal. Similar changes in physical properties were noted in coarse-grained cold-drawn and cold-rolled material.

TABLE V.—*Properties of some Coarse-grained Hot-rolled Sheet.*

Thickness, in.	E. L., lb per sq. in.	M. S., lb. per sq. in.	Elong., 2 in. per cent.	Grain-size, mm.
0.096	23,000	46,000	33	0.20
0.093	26,300	50,000	36	0.10
0.095	23,000	47,200	38	0.15
0.074	24,000	45,000	36	0.08
0.064	24,600	46,000	36	0.10
0.067	26,000	48,700	35	0.12
0.122	24,700	47,000	36	0.12

Time Effect.

The effect of increasing the time of annealing was investigated, but no increase in the grain-size due to prolonged annealing was found. Samples were annealed for varying periods of time up to eight hours. Some difference was noted in the time required for cold-drawn steel and for the light pressings. One half-hour was required to produce grain-growth in the drawn material, while in thin pressings a few minutes was sufficient.

Thermal Critical Points.

Thermal critical points were determined with a coarse-grained sample from a large pressing, the stock being half inch plate, basic open-hearth, 0.05 per cent carbon. The stock was originally of fine grain, but had become very coarse-grained during the pressing and annealing operations, the grains in some cases being as large as 0.9 mm. The Leeds and Northrup apparatus for the determination of transformation points was used for this purpose, the resistance being kept low in order to make small changes noticeable. A slight change was noted at the A_1 points. At about 775° C. (1430° F.) a marked change was found in the first heating curve, the differential marker leaving the field entirely. The Ac_3 point was very marked at about 910° C. (1670° F.). On cooling the transformation points were not so marked. The A_2 point appeared at about 880° C. (1615° F.) and the A_1 point at about 775° C. (1430° F.). The sample was reheated several times to note changes that might occur in the location or the intensity of the transformation points. The intensity of the points Ac_2 and Ac_3 was much diminished on the second heating, while that of the A_1 points remained about the same. The location of the various points was unchanged.

Coarse Crystallisation in Commercial Materials.

Sheet and Strip Steel.—The occurrence of a coarse-grained structure is common in both hot-rolled and cold-rolled annealed sheet. In the former no grain growth was found in sizes heavier than 0.130 in., but was rather common in all thinner sheet, including 0.065 in., the smallest size examined. This grain-growth was moderate in most cases, the grain-size usually being between 0.08 and 0.12 mm. diameter. In some instances, however, a more coarsely grained structure was noted, occasionally as large as 0.40 mm. diameter, usually in the heavier sizes. Sheet is, of course, subject to rapid cooling during the rolling operation, and the presence of coarse grains in the finished material is probably due to the temperature falling within the critical range before rolling is completed, grain-growth occurring during cooling in the stock pile or on annealing. No grain-growth was observed in the heavier materials such as hot-rolled rod, plate, or sheet bar, either after rolling or after annealing within the critical range. Further annealing within the critical range seemed to have no effect on the grain-size of the sheet investigated.

The grain-size noted in cold-rolled annealed sheet varied considerably, but where grain-growth was found, the size was generally coarser than in hot-rolled sheet. Grain-growth occurred in all sizes down to and including 0.040 in., the lightest gauge examined. Grains 0.50 mm. in diameter were noted occasionally.

In many cases where sheet is used for such operations as pressing, a considerable increase in the number of operations becomes necessary when the material is coarse-grained; frequently the grain-size may be so large that the steel will not endure even light operations. In such cases the material can be made available for use by annealing at about 790°C . (1450°F .); or in some cases a temperature just above 900°C . (1650°F .) may be required. When the operations have been laid out according to the requirements of normal metal, the adjustment required to handle the coarse-grained material may be the cause of considerable difficulty in production.

There is no convenient method by which the condition of sheet can be determined absolutely. Microscopical examination, together with a tensile test, will indicate to a certain degree the condition of the metal and serve as a guide to its probable action in practice. These tests cannot be an infallible guide, because the strain received may be too complex, or because the coarse structure may only occur here and there throughout the metal in certain areas that may or may not be located by the tests. Moderately coarse-grained sheet that gives perfect satisfaction in one case may be very unsatisfactory in another. In general, however, the tests mentioned will serve to indicate material of decidedly coarse grain and also material that has not been handled properly in rolling or annealing.

When methods by which grain-growth may be prevented or eliminated are known, the problem of prevention or elimination is narrowed to a proper selection of the method most applicable to the particular case. For example, with hot-rolled sheet prevention requires careful regulation of the finishing temperature, the reduction of area, and the annealing, if this operation be performed. When thin sheet is rolled, such regulation is exceedingly difficult. With cold-rolled sheet grain-growth can be eliminated by the use of heavy reductions, but here again other difficulties arise. Surface irregularities in the hot-rolled sheet and the difficulty of measuring exactly the gauge of large thin sheets makes an absolute determination of the reduction exceedingly difficult. Furthermore, a coarsely-grained structure may have been introduced in the hot-rolling. From these considerations it can readily be seen that while grain-growth may be prevented by the use of heavy reductions the application of this method is not always commercially practicable.

Grain-growth in sheet may be eliminated by annealing the hot-rolled sheet at a temperature somewhat above 900°C . (1650°F .), and if the sheet is then cold-rolled the temperature of the subsequent annealing should be kept below 650°C . (1200°F .). Sheet treated in this manner will be somewhat stiffer than the ordinary annealed cold-rolled sheet, but can be strained to a considerable degree before annealing becomes necessary. The difficulties in the annealing of sheet at the high temperature are obvious, but many of these may be eliminated by the use of box annealing. That this method is commercially practicable is shown by the fact that sheet treated in this manner is now furnished in the States, and gives excellent satisfaction in some decidedly difficult pressing operations. This sheet is box-annealed after hot-rolling at a temperature somewhat above 900°C . (1650°F .), is then cold-rolled and annealed just below 650°C . (1200°F .). As stated, sheet treated in this manner seems to be somewhat stiff, especially so when compared with coarse-grained sheet, which is almost always extremely pliable, but when tested in pressing operations excellent results were obtained, especially in the more difficult deep-drawing operations. The use of this material permitted the elimination of many of the annealing operations which had been found necessary with the material usually employed. In many cases the increased cost of sheet annealed to remove coarse crystallisation may be more than balanced by the elimination of much of the annealing usually required between operations and also by the increase in production obtained.

In cold rolled stripped steel, where the gauge can be

determined accurately and close control of the rolling is usually possible, grain-growth can be prevented by the use of reductions of area above 25 to 30 per cent. This ease of control and the general use of heavy reduction probably accounts in some measure for the superiority of strip steel over sheet in pressing operations.

Tube.—Low-carbon steel tube is, of course, subject to grain-growth under the same conditions as other low-carbon steel materials. In this investigation, however, no extreme grain-growth was found, although a certain amount was found in practically all the samples examined. The grain-size was usually not over 0.15 mm . diameter, and a temperature of 900°C . (1650°F .) was required in order to refine the structure.

Cold Pressings.—In certain pressing operations grain-growth may readily occur, causing serious difficulty in the process of manufacture or in service. Where steel 0.20 per cent or higher is used, grain-growth of a troublesome nature will rarely be found, but in many cases the use of this material is out of the question and a lower carbon steel is required, in which grain-growth can readily be produced. The occurrence of this grain-growth in pressings is dependent upon the nature of the operation and the annealing temperature. The annealing of pressings is a process that is frequently looked upon as requiring only elementary temperature control, the only consideration being that the metal reach a temperature high enough to remove the effect of cold work. The usual tendency is to raise the temperature to a point high enough to ensure proper softening of the metal, the temperature frequently reaching the critical range within which grain-growth occurs. In many pressing operations the amount of permanent deformation is relatively slight, and in such cases improper annealing may cause extensive grain-growth. Control of the annealing temperature is of the utmost importance in these cases. The selection of the proper annealing temperature depends to some extent upon the nature of the operation and the condition of the metal. Although annealing above 900°C . (1650°F .) or below 650°C . (1200°F .) will prevent grain-growth, the use of these temperatures is not always feasible. Annealing just below 690°C . (1275°F .) will usually produce grain-growth so slight that little trouble will occur in further operations. Such annealing will remove practically all the effect of cold work. In a few cases somewhat higher annealing temperatures are required, as, for instance, after certain upsetting operations which require temperatures somewhat above the critical point at 690°C ., and after a few pressing operations of a similar nature. (See J. F. Tinsley, "The Practical Importance of Heat Treatment in the Steel Wire Industry," American Iron and Steel Institute Meeting, May 22, 1914). In such cases, and also when it is necessary to refine a coarse-grained structure existing in the metal, the annealing temperature should be somewhat above the critical point at about 780°C . (1440°F .), or, if the partial refining occurring at this temperature is not sufficient to permit further operations, it should be raised above the critical point at about 900°C . (1650°F .).

Grain-growth of any extent can occur only when the strain received has been comparatively light, and control of this factor may prevent its occurrence. Increase in the extent or number of operations before annealing may often permit the use of almost any normal annealing temperature. Very often, however, the effect of the operation cannot be foretold, and occasionally some variation from normal conditions may occur, as, for instance, in the setting of the dye or punch, which will introduce comparatively light strains into some part of the pressing where such strains would be entirely unexpected under normal conditions. Furthermore, there are many operations which must necessarily be very light, and where annealing is required its proper regulations becomes essential. As it is in the earlier operations that grain-growth usually occurs, making further work on the material impossible until it has been properly annealed,

only a comparatively small proportion of the product will ordinarily find its way into use in a dangerously coarse-grained condition after ordinary pressing operations. In some cases, however, the presence of coarse crystallisation may not be detected in the manufacturing operations, and defective material may find its way into service. The cause of the trouble that may occur in many such cases is frequently obscure, as, for instance, in the occurrence of cracks in the blanked edges of pressings and around punched holes. In these cases in particular the cause may be traced to the pressure of the cutting edge in blanking or punching, subsequent annealing producing a moderately coarse-grained condition in a narrow layer following the line of pressure. Its presence may not be detected in the manufacturing operations, or perhaps the annealing is a final operation, so that no trouble develops until the pressing is placed in service. After a short time cracks appear along the edge or around punched holes and extend rapidly into the section. In a general way this condition has been observed by manufacturers of pressings, who occasionally find it necessary to grind the edges of certain pressings, in order to continue operations without the development of cracks. In service slight bending moments at the edges of pressings of this nature will cause the development of cracks.

Pressings which are to be carbonised and hardened should be heated to above 900° C. (1650° F.) during the carbonising process, to prevent or remove any coarse crystallisation. Distinction should be made here, of course, between the grain-growth occurring through a pressing operation and subsequent annealing and the grain-growth which may be developed through the use of high temperatures in the carbonising process.

General Methods of Prevention and Cure.

Many operations in the manufacture of low-carbon steel materials by means of cold work, especially in cold-pressing, are of such a nature that no annealing is required, and when eliminated no grain-growth can occur. In some cases, by slight changes in the methods of manufacture, annealing can be rendered unnecessary. When annealing is essential, the temperature must be carefully regulated and controlled. These considerations must be borne in mind by the user as well as the maker, for it may become necessary to apply further heat treatment to some material before it is put in service, and improper treatment may leave the material in a dangerous condition.

Where grain-growth has occurred and refining becomes necessary, heating above 900° C. (1650° F.) will bring about a complete refining of the grain. If the scale produced at this high temperature should be troublesome, the material may be quenched in water and subsequently annealed at 540–675° C. (1000–1250° F.) if necessary. A little concentrated hydrochloric acid thrown into the furnace at the start will permit ready removal of the scale. In some cases annealing at 790° C. (1455° F.) will produce a grain refinement sufficient to prevent further trouble.

Where annealing is necessary to remove the hardening effects of permanent deformation a temperature just below 690° C. (1200° F.) will usually give satisfactory results. In some cases a temperature of about 790° C. (1455° F.) may be required, and occasionally 900° C. (1650° F.) will be required. The choice of the annealing temperature depends upon the conditions existing in each case.

To summarise the foregoing, it may be stated that grain-growth in cold-worked low-carbon steel can be avoided by the application of comparatively heavy work to the metal before annealing, or by proper selection and control of the annealing temperature, according to the working conditions. If the metal is not annealed after the cold work no grain-growth can occur.

Conclusions.

1. Grain-growth in low-carbon steel will be produced by permanent deformation of the metal within certain limits, followed by annealing within certain temperature ranges.

2. The greater the amount of strain within these deformation limits, the smaller will be the grain-size produced by annealing.

3. The limits of the annealing range within which grain-growth due to permanent deformation will be produced are 650° and 900° C.

4. When the strain is less than a certain or "critical" amount, the annealing range within which grain-growth can occur seems to be limited by the thermal critical points at about 690° and 780° C.

5. The most practical standard by which to measure the permanent deformation, or strain beyond the elastic limit, seems to be the reduction of area. Experiments based upon measurements with this as a standard show that no grain-growth occurs following a reduction of area of less than about 7 per cent or more than about 25 to 30 per cent. The "critical" strain mentioned seems to be marked by a reduction of area of about 9 per cent.

6. The refining action taking place at about 780° C. is a further indication of the presence of a thermal critical point at this temperature.

7. The presence of carbon causes a suppression of grain-growth, an effect which, while negligible when the carbon content is low, is very pronounced when the steel contains 0.15 per cent or more. No noticeable grain-growth was found to occur in steels which were uniformly above 0.18 per cent in carbon content.

Discussion.

The PRESIDENT, in presenting the papers, said that experiments he was carrying out showed that far below 300° C. phenomena occurred in steel showing it not to be in a quiescent state. This fact was not properly appreciated, and it might explain why breakages often took place long after the material had been hardened. He wished Mr. Sherry had not confined himself to only one type of steel.

Dr. W. ROSENHAIN said Mr. Sherry's paper gave a new significance to the importance of "ghosts" in mild steel. In these relatively carbonaceous areas grain-growth could occur, and if this was facilitated by phosphorus the handling of mild steel needed careful watching. The annealing-point recommended (650° C.) was only safe in a material that did not rely on carbon content for the greater portion of its strength. It could be inferred from the paper that the theory of the existence of a thermal critical point at about 780° was far from dead.

ON THE RATES OF SOLUTION OF METALS IN FERRIC SALTS AND IN CHROMIC ACID.*

By R. G. VAN NAME and D. U. HILL.

(Continued from p. 11).

Tin.—Metallic tin was found to dissolve readily, retaining a clean bright surface, in the ferric sulphate solutions used. The results as recorded in Table IV. were calculated by using for the concentration of ferric salt the expression $C - c_0 - \frac{1}{2}(c - c_0)$, in which C and c_0 are the initial concentrations of ferric and ferrous salt respectively, and c is the titre of the solution at time t . This method of calculation is based on the reaction $2\text{Fe}^{+++} + \text{Sn} = 2\text{Fe}^{++} + \text{Sn}^{++}$; that is, it takes no account of the possibility of oxidation beyond the stannous stage.

The assumption here involved, that stannous sulphate is not oxidised by the ferric sulphate, may seem at first sight to be unwarranted, even as an approximation, for the reaction between stannous chloride and ferric chloride, as shown by the work of Kahlenberg (*Journ. Am. Chem. Soc.*, 1894, xvi., 314) and of A. A. Noyes (*Zeit. Phys. Chem.*,

* From the *American Journal of Science* xlii., 701.

TABLE IV.—*Fin.* $R'Fe(SO_4)_2$, 0.05 molar.

No. of expt.	H_2SO_4 , 5 molar.								K.
1.	C = 62.00	$c_0 = 2.46$							
	$v =$	580	560	540	520	500	480	460	
	$\Delta t =$	10	10	10	10	10	10	10	
	$c =$	5.91	9.48	13.00	16.53	20.13	23.80	27.40	
	$k_1 =$	1.71	1.75	1.71	1.71	1.75	1.78	1.72	
	$k =$	1.71	1.74	1.71	1.71	1.75	1.78	1.72	1.73
2.	$k =$	1.76	1.76	1.75	1.75	1.71	1.74	1.71	1.74
3.	$k =$	1.75	1.70	1.73	1.69	1.67	1.71	1.66	1.70
	H_2SO_4 , 0.25 molar.								
4.	$k =$	4.07	4.03	4.09	4.10	4.18	4.22	4.35	4.15
5.	$k =$	4.07	4.04	4.11	4.14	4.28	4.27	4.36	4.18

Initial Velocities by Extrapolation.—Expt. 4, 3.97; Expt. 5, 3.95.

TABLE V.— $R'Fe(SO_4)_2$, 0.05 molar.

No. of expt.	<i>Copper.</i>								K.
	H_2SO_4 , 0.25 molar.								
1.	$k =$	3.83	3.58	3.78	3.68	3.54	3.61	3.64	3.67
2.	$k =$	3.76	3.64	3.69	3.60	3.55	3.62	3.51	3.62
	H_2SO_4 , 1.25 molar.								
3.	$k =$	3.31	3.21	3.26	3.22	3.24	3.41	3.02	3.24
4.	$k =$	3.36	3.25	3.22	3.18	3.16	3.13	3.02	3.19
	H_2SO_4 , 5 molar.								
5.	$k =$	1.73	1.67	1.64	1.66	1.69	1.46	1.60	1.63
6.	$k =$	—	1.64	1.68	1.59	1.63	1.53	1.53	1.62
7.	$k =$	1.68	1.66	1.65	1.60	1.61	1.59	1.62	1.63
	<i>Silver.</i>								
	H_2SO_4 , 0.25 molar.								
8.	$k =$	1.60	1.60	1.44	1.34	1.29	1.19	1.08	1.36
	H_2SO_4 , 1.25 molar.								
9.	$k =$	1.61	1.49	1.35	1.36	1.23	1.14	1.18	1.34
10.	$k =$	1.61	1.53	1.48	1.41	1.29	1.27	1.15	1.39
	4 grms. Ag_2SO_4 added at the outset.								
11.	$k =$	0.73	0.63	0.62	0.59	0.56	0.52	0.41	0.58
	H_2SO_4 , 5 molar.								
12.	$k =$	1.28	1.16	1.11	1.08	1.06	1.06	1.05	1.11
13.	$k =$	1.25	1.16	1.17	1.10	1.04	1.05	1.02	1.11
	<i>Zinc.</i>								
	H_2SO_4 , 0.01 molar.								
14.	$k =$	4.41	4.32	4.35	4.56	4.56	4.57	5.00	4.46
15.	$k =$	4.27	4.38	4.13	4.07	4.48	4.34	4.39	4.29

Initial Velocities by Extrapolation.—Expt. 1, 3.75; Expt. 2, 3.73; Expt. 3, 3.27; Expt. 4, 3.33; Expt. 5, 1.74; Expt. 6, 1.70; Expt. 7, 1.69; Expt. 8, 1.67; Expt. 9, 1.61; Expt. 10, 1.65; Expt. 12, 1.23; Expt. 13, 1.24.

TABLE VI.

Metal.	Solution.		Single potential (volts).					
Silver	$1/20$ m. $KFe(SO_4)_2$, $1/4$ m. H_2SO_4 ,	$1\frac{1}{4}$						+0.937
	" " 5 "	$1\frac{1}{4}$						+0.919
	" " 1 "	$1\frac{1}{4}$						+0.883
	" " 1 " $1/200$ m. Ag_2SO_4	$1\frac{1}{4}$						+0.948
Copper	" " $1\frac{1}{4}$ "	$1\frac{1}{4}$						+0.540
	" " $1\frac{1}{4}$ "	$1\frac{1}{4}$						+0.525
	" " 5 "	$1\frac{1}{4}$						+0.508
	" " $1\frac{1}{4}$ " $1/100$ m. $CuSO_4$	$1\frac{1}{4}$						+0.549
Cadmium	" " $1\frac{1}{4}$ "	$1\frac{1}{4}$						-0.205
	" " $1\frac{1}{4}$ "	$1\frac{1}{4}$						-0.224
	" " 5 "	$1\frac{1}{4}$						-0.236
	" " $1\frac{1}{4}$ " $1/100$ m. $CdSO_4$	$1\frac{1}{4}$						-0.200
Silver	0.015 m. CrO_3 , $1/4$ m. H_2SO_4 ,	5						+0.968
	" " 5 "	5						+0.894
	" " 5 " $1/200$ m. Ag_2SO_4	5						+0.905

TABLE VII.— FeCl_3 , 0.05 molar.

No. of expt.		TABLE VII.—FeCl ₃ , 0.05 molar.								K.
Cadmium.										
HCl, 0.5 molar.										
1.	k =	4.17	4.08	4.16	4.16	4.13	4.18	4.20	4.15	
2.	k =	4.09	4.28	4.15	4.27	4.21	4.18	4.12	4.19	
HCl, 0.1 molar.										
3.	k =	4.32	4.16	4.37	4.12	4.14	4.25	4.29	4.24	
4.	k =	4.12	4.15	4.17	4.18	4.12	4.14	4.12	4.14	
Iron.										
HCl, 0.5 molar.										
5.	k =	4.26	4.30	4.29	4.15	4.39	4.50	4.41	4.33	
6.	k =	4.24	4.34	4.39	4.37	4.40	4.40	4.44	4.37	
HCl, 0.1 molar.										
7.	k =	4.18	4.10	4.18	4.35	4.18	3.83	4.22	4.15	
8.	k =	4.08	4.11	4.06	4.12	4.17	4.16	4.15	4.12	
Copper.										
HCl, 0.5 molar.										
9.	k =	4.26	4.22	4.32	4.42	4.33	4.49	4.41	4.35	
10.	k =	4.14	4.25	4.29	4.37	4.28	4.22	4.20	4.25	
HCl, 0.1 molar.										
11.	k =	3.43	3.28	3.26	3.17	3.16	3.09	2.99	3.20	
12.	k =	3.56	3.32	3.30	3.23	3.15	3.02	3.11	3.24	

Initial Velocities by Extrapolation.—Expt. 9, 4.20; Expt. 10, 4.20; Expt. 11, 3.40; Expt. 12, 3.48.

1895, xvi., 550), is fairly rapid and practically complete, and is, moreover, accelerated by hydrochloric acid. We have found, however, that under the conditions of our experiments the oxidation of stannous sulphate by ferric sulphate is extremely slow. The following observations will serve to illustrate this fact:—After an experiment on the rate of solution of tin, the solution remaining in the apparatus (and containing a large excess of ferric sulphate) was always found to give a brown precipitate with hydrogen sulphide, even after standing over night. Again, a mixture of stannous sulphate with a small amount of ferric sulphate, strongly acidified with sulphuric acid and coloured red by thiocyanate, retained its colour for many hours, but bleached rapidly as soon as a little potassium chloride was added, thus showing conspicuously the much greater velocity in the presence of chloride ion.

It is certain, therefore, that comparatively little stannic sulphate can have been formed during the short time occupied by the experiment (about seventy minutes). Nevertheless it is desirable to consider what effect the oxidation of the stannous sulphate by the ferric sulphate would tend to have upon the observed reaction velocity. The important point here is the fact that this reaction produces no change in the titre of the solution towards permanganate. Consequently, the analyses yield us no information concerning the extent to which ferric sulphate has been replaced by stannic sulphate, but give only the sum of the two. Both react with metallic tin, and with the same ultimate result so far as the yield of products which reduce permanganate is concerned, but the specific rates at which ferric sulphate and stannic sulphate, respectively, react with the metal, may be, and probably are, quite different. We may therefore conclude that the only direct effect on the observed reaction velocity to be expected in a case of this kind, due to the second stage of the reaction, is a downward or an upward trend of the velocity constants, according as the original oxidiser, or the one replacing it, reacts most rapidly with the metal. (It is evident that this will in many cases be determined more by rapidity of diffusion than by oxidising activity).

Experiments 1, 2, and 3 of Table IV. show no such trend in the constants, and the averaged values of k may accordingly be assumed to be practically free from error

due to the second stage of the oxidation. In Experiments 4 and 5 the constants show a slight rise, so that here the initial reaction velocities, obtained by linear extrapolation in the way described above, furnish the safest basis for comparison with the other metals, and will be so used. Whether the observed rise in the constants is due to the second stage of the reaction or to some other cause, no serious doubt attaches to the initial velocities, which are entirely consistent with the values given by the other metals.

Copper and Silver.—The results obtained with copper and with silver are much alike and can conveniently be considered together. They are recorded in Table V., together with two experiments on the rate of solution of zinc. The silver used was from a sample of high purity which gave no test for copper. For the copper discs the best obtainable grade of commercial sheet copper was employed, but the sample was not subjected to any special tests for purity. Both silver and copper retained a bright clean surface in dissolving in the ferric sulphate, but both gave in all cases velocity constants which decreased as the experiment progressed, though this effect was much more marked with silver than with copper.

For silver, at least, the explanation is clear, since the reaction between silver and ferric ion has been shown to be far from complete. Noyes and Brann (*Journ. Am. Chem. Soc.*, 1912, xxxiv., 1016) found that only about one-fourth of the ferric ion was reduced at 25°. The rate of the chemical reaction proper must therefore decrease with increase in the silver content of the solution, which accounts for the falling constants in our silver experiments. The correctness of this explanation is placed beyond question by Experiment 11, in which silver sulphate, added at the outset, produced a large decrease in the reaction velocity.

(NOTE.—A part of the silver sulphate added was still undissolved at the start, but dissolved during the course of the experiment. This was no doubt the cause of the falling constants).

By analogy, the decrease in the copper constants should be explainable in the same way. Electrochemical evidence tending to confirm this is found in Table VI., where it is shown that a copper electrode becomes more positive toward a solution of ferric sulphate when copper sulphate

is added, thus proving that the reaction is to some extent reversible. Silver and cadmium electrodes show a like behaviour. All potentials in the table are referred to the normal calomel electrode as +0.560 volts, but no corrections have been applied for diffusion potentials. The values lay no claim to accuracy, as the concentrations of the solutions were only approximate, and the potential readings changed somewhat with the time, but the effect of the added salts is unmistakable. It is also clear that the electrode in all cases becomes less positive or more negative to the solution as the acidity increases, a fact to which we shall have occasion to refer later.

The reaction between ferric ion and a metal would, in general, be expected to be more complete the less noble the metal, and this probably explains why the tendency of the reaction velocity to decrease during the course of the experiment, though large enough to affect the results in the case of silver and (to a smaller extent) also in the case of copper, was not appreciable with tin, nickel, iron, and cadmium.

On account of this decrease in the constants it is clear that the extrapolated initial velocities, in all the silver and copper experiments, are the values which properly represent the individual experiments.

Zinc.—For the experiments with zinc the metal used was the very pure commercial grade from the "Bertha" mine in Pulaski, Virginia. This was cast into thin plates and then ground and filed to the desired shape and thickness. Unfortunately it proved impossible to obtain the rate of solution of zinc free from the disturbing influence of an evolution of hydrogen, which was given off in appreciable quantity even in ferric sulphate solutions to which no acid had been added. It has been shown in a previous paper (*Am. Journ. Sci.*, xxxii., 217; see also *Ibid.*, xxxvi., 541) that the evolution of a gas tends to raise the observed reaction velocity, and by an uncertain amount, so that the velocity constants obtained in Expts. 14 and 15, in the presence of 0.01 molar sulphuric acid, are probably slightly too high.

These two experiments are the only ones recorded in this paper which are affected by this source of error. None of the other metals gave an appreciable evolution of hydrogen under the conditions of experiment.

Rates of Solution in Ferric Chloride.

No change in the conditions or general procedure described above for ferric sulphate was made in the experiments with ferric chloride, except that in making the titrations definite amounts of manganous sulphate, sulphuric acid, and phosphoric acid were added to the sample, instead of phosphoric acid alone. This modification, made necessary by the presence of chloride, involved a slight sacrifice in the accuracy of the analyses. Table VII. contains the results.

The experiments with cadmium call for no special comment. In the experiments with metallic iron the discs remained wholly free from the black coating formed in some cases in the sulphate solution. As before the expression $C - c_0 - \frac{2}{3}(c - c_0)$ was used in calculating the velocity constants for iron.

Copper dissolving in an acidified ferric chloride solution is oxidised in two stages, the case being therefore unlike that of copper in ferric sulphate, but closely analogous to that of tin in ferric sulphate. As in the latter case, the titre of the solution toward permanganate is not changed by the second stage of the oxidation, so that the analyses do not distinguish between ferric chloride and cupric chloride, but give their sum. The velocity constants have been calculated in exactly the same way as in the tin experiments. In fact, the sole difference between the two cases is that here the second stage of the reaction is comparatively rapid. A good deal of cupric chloride must therefore have accumulated in the solutions, reaching at the close of Experiments 9 and 10, in which this effect was largest, a concentration considerably larger than that of the ferric chloride itself.

It is evident that this substitution of cupric for ferric chloride would tend to cause a progressive change in the reaction velocity during the experiment. A careful consideration of the probable effect of the various factors influencing the result seems to show that such changes as those observed in Experiments 9 to 12, in which the direction of the change depends upon the acidity, are not incompatible with the point of view which we have adopted. We shall, however, make use of only the extrapolated initial velocities, so that the cause of the changes in velocity is for our purpose of minor importance.

To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, December 7, 1916.

Dr. ALEXANDER SCOTT, M.A., F.R.S., President,
in the Chair.

THE PRESIDENT referred to the loss sustained by the Society, through death, of Leonard de Koning, Charles Umney, and John Wrightson.

THE PRESIDENT also referred in sympathetic terms to the celebration of the centenary of Gerhardt, to be held by the Société Chimique de France on December 8, 1916, and, after giving a brief outline of Gerhardt's life and work, showed the far-reaching influence his investigations have had upon chemical science.

Mr. K. H. Vakil was formally admitted a Fellow of the Chemical Society.

Certificates were read for the first time in favour of Messrs. Charles William Brown Arnold, B.Sc., care of Messrs. Shaw, Wallace, and Co., Calcutta, India; Robert de la Poer Beresford, M.D., Derwent Grange, near Oswestry; Sir Hugh Bell, Bart., D.C.L., Rounton Grange, Northallerton; Henry Charles Stewart-Carlile, 27, Narcissus Road, West Hampstead, N.W.; John Ernest Dunstan, Ashdale, Gladiator Street, Honor Oak Park, S.E.; Reginald George Early, 6, Eliot Park, Lewisham, S.E.; John Fitzpatrick Ferns, M.Sc., 61, Withington Road, Whalley Range, Manchester; Gilbert Arthur Freak, B.Sc., Sudan Club, Khartoum, Sudan; William Douglas Graddon, B.Sc., 34, The Avenue, Muswell Hill, N.; Lionel Frederick Knapp, B.Sc., Hertcombe, Kingston Hill, Surrey; Trevor Owen Morgan, B.Sc., 14, Herbert Street, Blackley, Manchester; Hubert Sutton Patterson, 20, Sheen Road, Richmond, Surrey; John Nicholson Vowler, 54, Gondar Gardens, West Hampstead, N.W.

Messrs. G. Druce and E. A. Evans were elected Scrutators, and a ballot for the election of Fellows was held. The following were subsequently declared as duly elected:—Henry Vin Arny, Ph.D., Ph.G.; Frederick William Attack, M.Sc.Tech., B.Sc.; Syed Mahomed Azain, B.A.; Douglas Heriot Baird; Gerrard W. Baker; Satish Chandra Banerji, L.M.S.; Charles Samuel Bedford; William Alfred Benton; Stephen Bernard Bowyer; Ralph Eastace Brett; Leslie Norman Brown; Arthur Sidney Carlos, B.Sc.; Herbert Charles Cocks; Norman Cooke; Henry Edward Cox, B.Sc.; Alfred William John Denney; Arthur Fairbourne, M.Sc.; Alexej Eugrafovitch Favorsky; George James Francis; Daniel Gardner; Stanley Frederick Garrard, B.Sc.; Sir Robert Abbott Hadfield, D.Sc., F.R.S.; Archibald John Hall, B.Sc.; John Allen Harker, D.Sc., F.R.S.; William Charles Harris; Charles Harrison; Harry Hey; Cedric Stanton Hicks, M.Sc.; Herbert Hobson; Edward John Honess; Leo Fedorovitch Iljin; Percy Claude Cameron Isherwood, Ph.D.; Robert Smith Jackson; John Jacques; Albert Theodore Kremers; John Lea; George Lodge;

Francis Eric Milsom, B.Sc.; Burrows Moore, B.Sc.; Cosmo Murray; Thomas Needham; William George Palmer, B.A., B.Sc.; Richard Garnet Peaney; John Pomphrey; Arthur Walter Richardson; Arthur Villiers St. Armande; Herbert Savage, Sher Singh Sawhny, M.Sc., B.Sc.; Charles Adalbert Schunck; Neville Steele; Arthur George Surfleet; Edwin Taberner, B.Sc.; Crozier Fullerton Tofts; Frederick Alfred Unwin; Adolph William Henry Upton; Ernest Edward Wallen.

The following paper was read:—

"Spinacene: A New Hydrocarbon from certain Fish-liver Oils." By A. CHASTON CHAPMAN.

Ordinary Meeting, December 21, 1916.

Dr. ALEXANDER SCOTT, M.A., F.R.S., President,
in the Chair.

The PRESIDENT referred to the loss sustained by the Society, through death, of Prof. Thomas Purdie, LL.D., F.R.S., who was elected a Fellow on June 3, 1876, and who died on December 14. Prof. Purdie served on the Council from 1888 to 1892, and was Vice-President from 1899 to 1902.

The PRESIDENT announced that the Society had received a handsome present in the shape of an astronomical clock and barometer from Mrs. Meldola as a memorial of the late Prof. Raphael Meldola. The clock and barometer have been placed in the Hall.

The attention of Fellows was called to the Andrew Carnegie Research Scholarship Fund, from which a limited number of grants are made annually by the Council of the Iron and Steel Institute in aid of research work on problems of practical importance relating to the metallurgy of iron and steel and allied subjects.

Full particulars are given in the circular on the Notice Board or can be obtained from the Secretary of the Iron and Steel Institute, 28, Victoria Street, S.W.

Messrs. A. W. J. Denney and A. M. Wright were formally admitted Fellows of the Chemical Society.

Certificates were read for the first time in favour of Messrs. Charles William Dick, B.Sc., 8, Vicarage Road, Frindsbury, Rochester; Herbert Henry Froyssell, 66, Hartington Road, Liverpool; Arthur Austin Hoskings, Rainham, Kent; Jacob Kizewsky, 46, Roman Road, Victoria Park, N.E.; George Christie Redpath, 52, Eastbourne Gardens, Monkseaton, Northumberland; Arthur Stanley Reed, 6, Ellesmere Avenue, South Gosforth, Northumberland.

The following papers were read:—

"Studies on the Walden Inversion. Part V. The Kinetics and Dissociation Constant of α -Bromo- β -phenylpropionic Acid." By G. SENTER and G. H. MARTIN.

"The Alcohols of the Hydroaromatic and Terpene Series. Part III. The *iso*Pulegols Corresponding with *l*-Menthol and *d*-Neomenthol." By R. H. PICKARD, W. LEWCOCK, and H. DE PENNINGTON.

"Lead Sub-iodide, and an Improved Method of preparing Lead Sub-oxide. The Solubility of Lead Iodide." By H. G. DENHAM.

FARADAY SOCIETY.

Ordinary Meeting, December 18, 1916.

Sir ROBERT HADFIELD, F.R.S., President,
and subsequently

Prof. ALFRED W. PORTER, F.R.S., was in the Chair.

Mr. EZER GRIFFITHS and Mr. EDGAR A. GRIFFITHS (National Physical Laboratory) described and exhibited "A Carbon Tube Furnace for Testing the Softening Points and Compressive Strengths of Refractories."

The paper describes a carbon tube furnace designed for the testing of refractory materials under definite load.

The specimens are cut from the brick and ground up into the form of short cylinders. Pressure is applied by means of springs suitably connected to carbon rods which carry the specimen under test.

Two simple forms of electrode construction are described. In one of them the current is carried by two copper tubes bent into a zig-zag form and cast into two blocks of white bearing metal. The faces of the blocks are cast to the form of the carbon tube to which they are clamped. The copper tubes also serve for water cooling.

The temperature of the specimen is directly observed by means of a polarising type of optical pyrometer. For this purpose a slot $\frac{1}{8}$ in. wide extends the entire length of the tube. A slot was made in preference to a round hole, since the latter would have produced a discontinuity in the resistance of the tube.

The paper contains a number of references to publications on electric furnaces and refractories.

Dr. W. ROSENHAIN remarked that the results obtained depended upon the surfaces between the little columns being absolutely true. In the case of a material which softened with temperature the results would be affected by the intensity of the pressure.

Mr. H. M. RIDGE said he was glad to know of an apparatus that could be subjected to over 1500° C. and at the same time give accurate tests of firebrick materials. He hoped that if comparative tests had been made on the standard bricks they would be published. The recent regulation fixing a maximum price for firebricks militated against the good brick, but enabled the maker of inferior bricks to raise his prices. The use of an apparatus like that described would enable a sliding scale to be fixed on a basis of actual tests.

Dr. H. BORNS asked how long a test took.

Dr. H. C. GREENWOOD asked whether tests had been made on the effect of temperature on tensile strength.

Dr. R. LESSING thought the test pieces used in the furnace rather too small, especially for large-grained material.

Mr. E. GRIFFITHS, in reply, said there was no difficulty in applying the pressure normally. Usually three specimens were taken from a brick and the results only accepted when concordant. A small test-piece ensured uniform distribution of temperature. A test usually took two hours and a half at a 10° C. increase of temperature per minute. Comparative tests could not be published at present, but he might say that a magnesite brick broke down at 1500 C. when heated uniformly, under a pressure of about 30 lb. This was about the normal.

The President presented a paper by Prof. E. D. CAMPBELL (University of Michigan) entitled, "*Do Equiatomic Solutions in Iron possess Equal Resistances?*" (Will be inserted in full).

The President also presented a paper by Mr. RALPH H. SHERRY, M.A. (Detroit, U.S.A.), on "*Grain-growth in Deformed and Annealed Low Carbon Steel.*" (Inserted in full).

A paper by Mr. R. G. PARKER and Mr. A. J. DALLADAY on "*The Union of Glass in Optical Contact by Heat Treatment*" was read by Mr. Dalladay. (Already inserted).

Dr. W. ROSENHAIN regarded the authors' results as a remarkable achievement. He thought that various methods of polishing might make a difference in the behaviour of the glass. He discussed the behaviour of moisture or hydrated films as affecting the union. Might not chemical cleaning give better results than mechanical?

Prof. ALFRED W. PORTER thought the fact that the outside surface film of the glass was in a totally different condition from that of the inside was responsible for the possibility of the process. The outside film would be practically in a flowing state.

Mr. J. A. DALLADAY, in reply, said chemical cleaning might be useful, but it had not when tried given good results. Such trouble as occurred was caused by little

pieces of cellulose left from the material used for wiping the surface.

A paper by Prof. W. C. McCULLAGH LEWIS (University of Liverpool) on "The Effect of Pressure on the Equilibrium Constant of a Reaction in a Dilute Solution: A Simple Proof of the Expression," was presented by Prof. Alfred W. Porter, in the absence of the Author.

The paper indicates a simple mode of deducing the effect of external pressure on the equilibrium constant of a reaction in dilute solution. The method, which involves the simple concept of maximum work, may be found to be of use by teachers of physical chemistry, as students generally find the method of Planck somewhat difficult.

At the conclusion of the meeting the Secretary announced that early in the New Year a General Discussion, to be opened by Sir George Beilby, F.R.S., would be held on "The Training and Work of the Chemical Engineer."

Later in the Session General Discussions would probably be arranged to deal with "Osmotic Pressure" and "The Setting of Cements and Plasters."

Annual General Meeting, December 18, 1916.

The following Officers and Council were elected:—

President—Sir Robert Hadfield, F.R.S.

Vice-Presidents—Prof. K. Birkeland; W. R. Bousfield, K.C.; Prof. F. G. Donnan, F.R.S.; Dr. Eugene Haanel; Prof. A. K. Huntington; Dr. T. Martin Lowry, F.R.S.

Treasurer—F. Mollwo Perkin, Ph.D.

Council—W. R. Cooper; Dr. C. H. Desch; Dr. J. A. Harker, F.R.S.; Emil Hatschek; Cosmo Johns; Prof. Alfred W. Porter, F.R.S.; E. H. Rayner; A. Gordon Salamon; Dr. George Senter; Cav. Magg. E. Stassano.

The Report of the Council states that in spite of difficulties consequent on the war, it was found possible to hold two General Discussions in the year under review, one on "The Transformation of Pure Iron" and the other on "The Corrosion of Metals, Ferrous and Non-Ferrous." The published reports of these Discussions will be of particular value in focusing attention on some of the outstanding gaps in our existing knowledge of these important subjects. Indeed, the Symposium on Corrosion has been characterised in an American journal as the most valuable collection of papers that has yet appeared on this subject in England.

On account of disturbed financial conditions the American Electrochemical Society will in future only distribute to those of its members who pay an increased subscription the *Transactions of the Faraday Society*. The Council of the Faraday Society hope, however, to be able to purchase the *Transactions of the American Society* at cost, and distribute them to members without an increased subscription. This will involve the Society in a considerable extra expenditure, to cover which it is earnestly hoped there may be a substantial increase in the membership of the Society.

The Report indicates that the Society has been able to be of some service to the Government in connection with the war, and it states that besides those of its members who are on active service, a very considerable number of the officers and members are serving on the various Government Boards and Panels that have been constituted since the beginning of the war by the Admiralty, Ministry of Munitions, and Board of Education.

Lecture.—Colonel C. T. Heycock, M.A., F.R.S., will deliver a lecture entitled, "Alloys of Copper and Tin, Aluminium and Gold," at the Ordinary Scientific Meeting of the Chemical Society on Thursday, January 18, at 8 p.m.

NOTICES OF BOOKS.

Elementary Practical Chemistry. Part II. Analytical Chemistry, Qualitative and Quantitative. By FRANK CLOWES, D.Sc., Lond., and J. BERNARD COLEMAN, A.R.C.Sc. Eighth edition. London: J. and A. Churchill. 1916. Pp. xv.+255. Price 3s. 6d. net.

THERE is no better laboratory guide for students than this book, which has met with well-deserved success. It can be used equally profitably by beginners and more advanced students, and its use will ensure the laying of a particularly thorough foundation in practical chemistry. Both qualitative and quantitative analysis are treated, and in addition some preparations are described, to be performed at various stages of the student's work. They include general methods of obtaining salts, oxides, &c., and some miscellaneous preparations of peculiar interest, or such as involve the employment of special methods. The only defect of the book is the rather free use of small print in many of the separation tables and in the descriptions of some of the more advanced tests and experiments.

Text-book of Elementary Chemistry. By F. MOLLWO PERKIN, Ph.D., F.I.C., F.C.S., and ELEANOR M. JAGGERS. London: Constable and Co., Ltd. 1916. Pp. vii.+384. Price 3s. net.

THIS book contains a satisfactory course of elementary chemistry, although it does not differ essentially from others of the same type. It seems probable that the beginner's interest would be aroused by it, and he would certainly acquire a good deal of valuable information from it. The first two chapters describe physical experiments in thermometry, the determination of constants, &c., passing on to the investigation of the properties of the atmosphere. The atomic theory is introduced quite early in the course—a wise procedure, for if the student is thinking about his work and not regarding the experiments he performs merely as a series of spectacular effects he very soon wants explanations and generalisations, without which he is very likely to form hazy and erroneous ideas of his own. The book includes a short treatment of the metals, and a very useful chapter on technical processes, which can profitably be studied in outline by those who have worked through the preceding chapters. Among these are the manufacture of soap, coal-gas, aniline dyes, the distillation of oils, &c., and short readable accounts are provided of the main features of the processes employed.

Welfare Work. By E. DOROTHEA PROUD, B.A. (Adel.). London: G. Bell and Sons, Ltd. 1916. Pp. xx.+368. Price 7s. 6d. net.

THE foreword to this book, contributed by Mr. Lloyd George, emphasises the importance of welfare work in its effects upon national health, the output of factories, and the raising of the standard of efficiency. The author of the book is an Australian who has had unique opportunities of acquiring a knowledge of the subject, both in Australia and in England; she has served in the Welfare Department at the Ministry of Munitions since its foundation, but does not touch upon her work there, for the book was practically completed before the Department began work. She obviously brings wide sympathy, clear insight, and an unbiased judgment to bear upon the subject, and the book will be of inestimable value to those who are interested or engaged in welfare work. The growth of the movement in England is first described, and then the improvement of industrial conditions, wages, hours of employment, and the scope of the Welfare Department are discussed with the amount of detail which the importance of the subject demands.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxliii., No. 17, October 23, 1916.

Chemical Action of Sodium Peroxide on Sulphuretted Hydrogen.—C. Zenghelis and Stavros Horsch.—When a current of nitrogen is first passed through a combustion-tube containing peroxide and then a current of sulphuretted hydrogen, an energetic reaction occurs. The temperature rises and the peroxide becomes incandescent and fuses. The reaction is still more violent if the peroxide is previously heated, and in that case a flame is produced. In presence of air the sulphuretted hydrogen burns. The products depend upon the conditions of the reaction, differing according as much or little air is present or none at all, &c. The hydrogen always burns, forming water, which then attacks the peroxide, giving a complicated reaction. If the action occurs in an atmosphere of nitrogen sulphides and polysulphides of sodium are formed. A small quantity of sulphur is oxidised by the oxygen set free from the peroxide, giving thiosulphate and sulphate. If the current of hydrogen is sufficiently strong a small quantity of sulphur appears on the walls of the tube. If the reaction occurs in presence of a large quantity of air a loud detonation is produced; sulphate and free sulphur are produced, but no sulphide.

No. 18, October 30, 1916.

Semicarbazones of α -Ketonic Acids. α -Di-iodo and Di-bromo-phenylbutyric Acids; α -iodo and bromo-phenylcrotonic Acids.—J. Bougault.—By the action of iodine upon a very alkaline soda solution of the semicarbazone of benzylpyruvic acid, α -di-iodo-phenylbutyric acid is deposited as the sodium salt. The free acid fuses at 145°. It is insoluble in water and very soluble in alcohol and ether. The two isomeric (stable and labile) α -iodo-phenylcrotonic acids remain in the mother-liquors in the above reaction. They are also obtained by decomposing the α -di-iodo acid by means of a weak alkali solution such as sodium acetate. α -Dibromo-phenylbutyric acid may be obtained by the action of sodium hypobromite upon the semicarbazone of benzylpyruvic acid and can be isolated owing to the slight solubility of its sodium salt. The free acid fuses at 131° and possesses the general properties of the corresponding iodine compound. The α -bromo-phenylcrotonic acids are prepared in the same way as the iodo derivatives. These halogen acids can readily be converted into a β phenylcrotonic acid, otherwise prepared only with difficulty.

No. 19, November 6, 1916.

Atomic Weight of Lead.—Oechsner de Coninck and M. Gérard.—The authors have determined the molecular weight of lead oxide, and thence deduced the atomic weight of lead. They purified the lead by repeated treatment with the appropriate acid liquids and finally treated with a purified nitric acid, thus getting pure lead nitrate. If p is the weight of nitrate used and p' that of the oxide obtained by calcination, then the molecular weight of the oxide is given by the equation $\frac{p}{p'} = \frac{x + 108}{x}$. The mean of

our experiments gave as the atomic weight of lead 206.98. The International Commission in 1904 adopted the value 206.90. Lead extracted from uranium minerals gave the number 206.71, which agrees very well with the value found by Hönigschmidt and Horowitz, viz., 206.73.

Bulletin de la Société Chimique de France.
Vol. xix.-xx., No. 10, 1916.

Saponification of Some Pyrrol-dicarboxylic Ethers at 50°.—G. Korschun and A. Gounder.—The authors have studied the saponification at 50° of various pyrrol dicarboxylic ethers, and give in tabular form the data they have accumulated. The ethers studied include di- and tri- methyl, ureido-dimethyl, phenyl dimethyl, and diphenyl derivatives, and the amount of potash necessary to saponify one carboxethyl group is given in each case.

Cacodylate of Piperazine.—M. Astruc.—It is possible to bring about the combination of piperazine with a weak acid such as cacodylic acid. An aqueous solution is made of one molecule of piperazine and two of cacodylic acid, and evaporation is allowed to proceed first on the water-bath and then in vacuo till crystals separate. The substance is colourless and very deliquescent; the small crystals contain four molecules of water of crystallisation. The composition of piperazine cacodylate is represented

by $\left(\text{As} \begin{array}{c} \text{OH} \\ \diagup \\ \text{CH}_3 \\ \diagdown \\ \text{CH}_3 \end{array} \right)_2$. It is acid to phenolphthalein and alkaline to helianthine.

Phosphorus Contained in Animal Proteic Matter after Demineralisation.—L. Lindet.—The calcination of a proteic substance shows that the ash contains the elements of calcium phosphate. From the study of white of egg, milk, blood, &c., the author has drawn the conclusion that only the matter which is insoluble in water and in salt solution contains organic phosphorus, while the soluble matter contains its phosphorus exclusively in the mineral state. Moreover, the substances rich in organic phosphorus form the organs which are most essential to life and those in which the daily transformations are most profound.

MISCELLANEOUS.

The New Denaturalising Material for Spirit Introduced in Norway.—Mr. Einar Simonsen, Chemist, of Kristiania, has found a new and improved method of denaturalising spirit by means of a distillate of crude petroleum (preferably Roumanian) up to 300° C. added in a degree of $\frac{1}{2}$ to 1 per cent. The method, which has already been experimentally tried in Norway for more than eighteen months, has proved quite satisfactory for its purpose. It is quite as safe against misuse as the method before used (methyl alcohol and pyridin); it has no disagreeable smell, but an unpleasant taste. For varnish one could up to now not use denaturalised spirit in the usual form, but had to use spirit which was only partly denaturalised. This specially denaturalised spirit had to be under the control of the authorities. This will no longer be necessary. The Norwegian Government has, therefore, after the most thorough examination and after the successful experience they have gained from Spirit-denaturering, bought the licence for the whole of Norway and introduced the method officially. The new method is much cheaper than any method before used.

MEETINGS FOR THE WEEK.

TUESDAY, 16th.—Royal Institution, 3. "The Old Brain and the New Brain, and their Meaning," by Prof. C. S. Sherrington.

THURSDAY, 18th.—Royal Institution, 3. "The Strength and Weakness of Romantic Poetry," by Prof. Sir Walter Raleigh.

— Royal Society of Arts, 4.30. "Between the Tigris and the Indus," by Col. Sir Thomas Holdich.
— Chemical Society, 8. "Alloys of Copper and Tin, Aluminium and Gold," by Col. C. T. Heycock.

FRIDAY, 19th.—Royal Institution, 5.30. "Soap Bubbles of Long Duration," by Prof. Sir James Dewar.

SATURDAY, 20th.—Royal Institution, 3. "The Lakes and Mountains of Central Africa," by A. R. Hinks.

THE CHEMICAL NEWS

VOL. CXV., No. 2982.

PALM KERNEL CAKE, PALM KERNEL MEAL, AND COCOANUT CAKE, COMPARED WITH SOYA CAKE FOR FATTENING CATTLE, YOUNG STORE CATTLE, AND FATTENING SHEEP, 1915-16.*

REPORT by Prof. DOUGLAS A. GILCHRIST, M.Sc.,
Director on behalf of Armstrong College, Newcastle-upon-Tyne,

TABLES I., II., III., and IV. contain summarised particulars of the results. The cattle and sheep were arranged in lots as described in the last-issued feeding trials bulletin (No. 23).

Summary Results with Fattening Cattle.—Tables I. and II. show the following average gains per week:—

	Standard ration.	Palm kernel cake ration.	Palm kernel meal ration.	Cocoonut cake ration.
	Lbs.	Lbs.	Lbs.	Lbs.
Bullocks ..	16'50	12'44	14'19	15'70
Heifers ..	8 92	10'00	9'25	7'42
Average ..	12 71	11'22	11'72	11'56

These average gains are very close to each other. It was anticipated that palm kernel meal might not be readily

Summary Results with young Store Cattle.—Better average gains were given by those wintered inside than those wintered outside, but at the end of March practical valuers attached 30s. a head more value to those wintered outside, as they had better coats of hair and were more promising grazing cattle. Palm kernel meal gave better results than palm kernel cake with these young cattle, although the meal contained less than 2 per cent of oil and the cake nearly 6 per cent. The gains per week were quite satisfactory for such store cattle in winter, and each lot came through the winter well. (See Table III.).

Summary Results with Fattening Hogs.—The sheep used were three-parts bred hogs, and had been bred near Rothbury in 1915. All the lots made satisfactory gains, which indicated that palm kernel cake and palm kernel meal are suitable foods for fattening sheep. Again palm kernel meal gave a better result than palm kernel cake. (See Table IV.).

The fattening bullocks made average net gains of from £3 to £6 a head; their live weight value increased from 47s. to 62s. a cwt. during the fattening period. The fattening heifers made average net gains of 50s. to 64s. a head. The net gains per head for the stirks varied from 10s. to 23s., and their value as stores increased from 42s. 6d. a cwt. at the beginning of the winter to 48s. at the end. The fattening hogs made net gains per head of from 3s. to 5s., and improved in live weight value from 5½d. to 6½d. a lb. during the fattening period.

The Chairman of the Colonial Office Committee on Edible and Oil Producing Nuts and Seeds (Mr. A. D. Steel Maitland, M.P., Under Secretary of State for the Colonies) wrote on August 14, 1915, that his Committee would be very glad if the experiments now completed at Cockle Park, as well as other trials at Offerton Hall and

COMPOSITION OF THE FOODS USED IN THE TRIALS.

By S. H. COLLINS, M.Sc., F.I.C., Lecturer and Adviser in Agricultural Chemistry, Armstrong College.

Constituents, per cent—	Soya cake.	Egyptian cotton cake.	Cocoonut cake.	Palm nut cake.	Palm kernel meal.	Maize
Moisture	10'40	11 60	11'65	11'00	12'40	14'30
Oil	6'03	4'07	8 37	5'40	1'35	4'54
Albuminoids	43 85	24'30	21'75	21'00	18 81	9 89
Carbohydrates	29 97	34'33	41 96	43'12	40'94	68'20
Fibre	4 63	20'15	10 75	15'78	22 60	1'47
Ash	5'15	5'55	5 52	3 70	3 90	1 60
	100'00	100 00	100'00	100'00	100'00	100'00
Nitrogen	7'02	3 89	3'48	3'36	3'01	1'58
Sand	0'65	0 70	1'05	0'75	0'80	None
Digestible oil	5'5	3 8	8 1	5 2	1'3	4 0
Digestible true albuminoids	37'7	19'9	16'5	17'5	15'6	6 7
Digestible carbohydrates and fibre	21 6	28'6	41'5	46 1	49'4	65 4
Starch equivalent	67	47	80	75	66	82
Price (per ton)	£12	£10	£11	£10	£9 15s.	£12

Seeds hay was valued at £4 and swedes at 12s., both per ton.

taken by the cattle and sheep in the dry state, but this was not so. The results are of a satisfactory character, and show that each of the new foods are valuable additions to our feeding stuffs. Care was taken that if any animal left any of the cake or meal this was removed. This is an important precaution in introducing any new foods. The cakes and meal were kept in the granary, and were in quite good condition after being stored for some months.

In some previous trials palm kernel cake gave the cattle more glossy coats and more "bloom," but in these trials no such effect was produced on the fattening cattle or on the young stirks.

at Newton Rigg, could be proceeded with, and also if the results might be reported to his Committee when the trials had been completed.

Sir Owen Philipps, K.C.M.G., M.P., a member of the Oil Producing Nuts Committee, has taken great interest in the progress of these trials and presented to the Cockle Park Committee 4 tons of palm kernel cake (from the African Oil Mills Co., Ltd., Liverpool) and 2½ tons palm kernel meal (from the Premier Oil Extracting Co., Ltd., Stoneferry, Hull) for these trials.

In 1913 over 234,000 tons of palm kernels were exported from British West Africa, of which over 181,000 tons went to Germany and about 40,000 tons to this country; and in 1912 over 50,000 tons of the same were exported from French West Africa, of which about 43,000 tons went to

* Bulletin No. 25, County Agricultural Experiment Station, Cockle Park. Issued by the County of Northumberland Education Committee.

TABLE I.—Feeding Experiments with Cattle Eighteen to Twenty-four Months Old, 1915-16.

Three Blue-grey Bullocks in each Lot. Daily Feeding Rations per 1000 lbs. Live Weight.

	LOT I. 78 lbs. swedes, 14 lbs. seeds hay, 2½ lbs. soya cake. 4 lbs. Egyptian cotton cake. (a) ½ lb. maize. cwt. qrs. lbs.	LOT II. 70 lbs. swedes, 14 lbs. seeds hay, 2½ lbs. soya cake. 4 lbs. palm kernel cake. (a) cwt. qrs. lbs.	LOT III. 76 lbs. swedes, 14 lbs. seeds hay, 2½ lbs. soya cake. 4 lbs. palm kernel meal. (a) cwt. qrs. lbs.	LOT IV. 70 lbs. swedes, 14 lbs. seeds hay, 2½ lbs. soya cake. 4 lbs. coconut cake. (a) cwt. qrs.
Average fasted live weight per head—				
At beginning of preliminary period, Nov. 5, 1915	7 2 1	7 1 18	7 1 23	7 2
Increase during preliminary period ending Dec. 8, 1915	0 2 4	0 1 24	0 1 25	0 2
Increase during first experimental month ending Jan. 5, 1916	0 3 1	0 1 26	0 1 21	0 1 5
Increase during second experimental month ending Feb. 2, 1916	0 2 13	0 1 24	0 2 3	0 2 22
Increase during third experimental month ending March 1, 1916	0 1 27	0 1 20	0 1 11	0 1 11
Increase during fourth experimental month ending March 29, 1916	0 1 27	0 1 17	0 2 24	0 2 13
Total gain per head during four months' trial ..	2 1 12	1 3 3	2 0 23	1 3 23
Average fasted live weight at end of trial ..	10 1 17	9 2 18	9 3 23	10 0 0
AVERAGE INCREASE PER HEAD PER WEEK	16'50	12'44	14'19	13'7
	£ s. d.	£ s. d.	£ s. d.	£ s. d.
Average value per head—				
At beginning of trial, at 47s. a cwt.	18 18 1	18 10 1	18 12 7	18 18 1
At end of trial, at 62s. a cwt.	32 5 0	29 19 0	30 17 3	31 0 0
AVERAGE INCREASE IN VALUE PER HEAD	13 6 11	11 9 0	12 4 8	12 1 11
Cost of food during four months' trial	9 1 7	8 6 8	8 5 1	8 11 8
Difference—Gain, less other expenses	4 5 4	3 2 4	5 19 7	3 10 3

(a) For 1 lb. of each of these foods ½ lb. soya cake and ½ lb. maize meal was substituted in the third and fourth months as the cattle were not taking quite well to the new foods.

TABLE II.—Feeding Experiments with Cattle Eighteen to Twenty-four Months Old, 1915-16.

Three Blue-grey Heifers in each Lot. Daily Feeding Rations per 100 lbs. Live Weight.

	LOT I. 78 lbs. swedes, 14 lbs. seeds hay, 2½ lbs. soya cake. 4 lbs. Egyptian cotton cake. (a) ½ lb. maize. cwt. qrs. lbs.	LOT II. 70 lbs. swedes, 14 lbs. seeds hay, 2½ lbs. soya cake. 4 lbs. palm kernel cake. (a) cwt. qrs. lbs.	LOT III. 76 lbs. swedes, 14 lbs. seeds hay, 2½ lbs. soya cake. 4 lbs. palm kernel meal. (a) cwt. qrs. lbs.	LOT IV. 70 lbs. swedes, 14 lbs. seeds hay, 2½ lbs. soya cake. 4 lbs. coconut cake. (a) cwt. qrs. lbs.
Average fasted live weight per head—				
At beginning of preliminary period, Nov. 5, 1915	7 0 3	7 0 11	7 0 9	7 0 5
Increase during preliminary period ending December 8, 1915	0 2 7	0 2 7	0 0 27	0 0 23
Increase during first experimental month ending Jan. 5, 1916	0 0 16	0 1 4	0 1 1	0 1 6
Increase during second experimental month ending Feb. 2, 1916	0 1 27	0 1 27	0 1 19	0 1 3
Increase during third experimental month ending March 1, 1916	0 1 8	0 1 5	0 1 6	0 0 24
Total gain per head during three months' trial ..	0 3 23	1 0 8	0 3 26	0 3 5
Average fasted live weight at end of trial ..	8 2 5	8 2 26	8 1 6	8 0 5
AVERAGE INCREASE PER HEAD PER WEEK	8 92	10	9'25	7'42
	£ s. d.	£ s. d.	£ s. d.	£ s. d.
Average value per head—				
At beginning of trial, at 47s. a cwt.	17 16 8	18 0 0	17 4 1	17 0 9
At end of trial, at 62s. per cwt.	26 9 9	27 1 6	25 14 10	24 18 9
AVERAGE INCREASE IN VALUE PER HEAD	8 13	9 1 0	8 10 9	7 18 0
Cost of food during three months' trial	5 19 1	6 16 11	5 11 4	5 8 5
Difference—Gain, less other expenses	2 14 0	3 4 1	2 19 5	2 9 7

(a) For 1 lb. each of these food-stuffs, ½ lb. soya cake and ½ lb. maize meal was substituted in the third month, as the cattle were not taking quite well to the new foods.

TABLE III.—Feeding Experiments with Cattle just over Six Months Old, 19 5-16.

Eleven Stirks in Lot I., Five in Lot II., and Six in Lot III.

The Average Daily Rations per 500 lbs. Live Weight during Sixteen Weeks were—

	Lot I.—Wintered outside. 10½ lbs. seeds hay, ¼ lb. soya cake 2½ lbs. palm kernel cake. cwt. qrs. lbs.			Lot II.—Wintered outside. 10½ lbs. seeds hay, ¼ lb. soya cake. 2½ lbs. palm kernel meal. cwt. qrs. lbs.			Lot III.—Wintered inside. 25 lbs. swedes, 6 lbs. seeds hay 1 lb. soya cake. 2 lbs. palm kernel cake. cwt. qrs. lbs.		
Average fasted live weight per head—									
At beginning of first experimental period, Dec. 7, 1915	4	2	12	4	2	1	4	2	11
Increase during first experimental period ending Feb. 2, 1916	0	1	27	0	2	19	0	2	11
Increase during second experimental period ending March 28, 1916	0	2	8	0	2	21	0	3	26
Total gain per head during sixteen weeks' trial.	1	0	7	1	1	12	1	2	9
Average fasted live weight at end of trial	5	2	20	5	3	13	6	0	20
AVERAGE INCREASE PER HEAD PER WEEK			7'44			9'5			11'06
	£	s.	d.	£	s.	d.	£	s.	d.
Average value per head—									
At beginning of trial, at 42s. 6d. a cwt.	9	16	1	9	11	11	9	15	8
At end of trial, at 48s. a cwt.	13	12	2	14	1	7	14	16	7
AVERAGE INCREASE IN VALUE PER HEAD	3	16	1	4	9	8	5	0	11
Cost of food during sixteen weeks' trial	3	6	1	3	6	5	4	10	10
Difference—Gain, less other expenses	0	10	0	1	3	3	0	10	1

TABLE IV.—Feeding Experiments with Sheep in Sheephovse, 1915-16.

Sixteen Three-parts Bred Hogs in each Lot. Daily Feeding Rations per 100 lbs. Live Weight. (a)

	Lot I. 8 lbs. swedes, 1½ lbs. seeds hay, 2½ lb. soya cake, 2½ lb. Egyptian cotton cake, ¼ lb. maize meal, lbs.			Lot II. 7½ lbs. swedes, 1½ lbs. seeds hay, 2½ lb. soya cake, ½ lb. palm kernel cake. lbs.			Lot III. 8 lbs. swedes, 1½ lbs. seeds hay, 2½ lb. soya cake, ½ lb. palm kernel meal, lbs.		
Average fasted live weight per head—									
At beginning of preliminary period, Nov. 18, 1915	82	13		82	06		82	06	
Increase during preliminary period ending Dec. 6, 1915	4	94		7	69		6	25	
Increase during first experimental month ending Jan. 3, 1916	5	13		4	44		3	88	
Increase during second experimental month ending Jan. 31, 1916	6	25		5	94		5	81	
Increase during third experimental month ending Feb. 28, 1916	10	5		11	19		12	94	
Total gain per head during three months' trial..	21	87		21	56		22	63	
Average fasted live weight at end of trial	108	94		111	13		110	94	
AVERAGE INCREASE PER HEAD PER WEEK	1	82		1	80		1	89	
	£	s.	d.	£	s.	d.	£	s.	d.
Average value per head—									
At beginning of trial, at 5½ d. per lb.	1	19	11	2	1	2	2	0	6
At end of trial, at 6½ d. per lb.	2	19	0	3	0	2	3	0	1
AVERAGE INCREASE IN VALUE PER HEAD	0	19	1	0	19	0	0	19	7
Cost of food during three months' trial	0	16	0	0	14	6	0	14	7
Difference—Gain, less other expenses	0	3	0	0	4	6	0	5	0

(a) As the hogs were not making satisfactory gains, ½ lb. maize meal was added to each ration in the third month, with excellent results.

Germany and about 3500 tons to this country. Up till the outbreak of war the industries dependent on these kernels were practically in German hands. Oil from palm kernels is used largely for the production of margarine, and is now invaluable for this purpose in this country. The Colonial Office Committee has recommended the imposition in the several West African Colonies of an export duty of not less than £2 a ton on all palm kernels exported from British West Africa, the duty to continue during the war and for five years afterwards, and to be remitted on all kernels

shipped to, and crushed in, any part of the British Empire. This recommendation is now before the Legislative Councils of the various West African Colonies, and is likely to be put into operation shortly. The importance, therefore, of testing palm kernel cake as a feeding material for cattle and sheep is evident, especially when there is a deficiency of other foodstuffs. Palm kernel meal is found to be an excellent basis for a pig meal, and as more oil is obtained from palm kernels by means of the extraction process of which palm kernel meal is the by-product, it

was also of the greatest importance to test extracted palm kernel meal as a feeding stuff.

On the averages of the years 1912 and 1913, Germany imported the following:—248,000 tons of palm kernels; 109,000 copra (the dried fleshy part of coconuts); 445,000 tons linseed and linseed meal; 217,000 tons cotton-seed; 123,000 soya beans; and 84,000 tons peanuts (earthnuts). Considerable quantities of these (especially of palm kernels) are now diverted to this country, and it is of the greatest importance that the British farmer should become familiar with the by-products produced from them.

Difficulty in some instance has been experienced with palm kernel cake not keeping well, but this difficulty did not arise last winter at Cockle Park. The cakes, kept in an ordinary granary, were in quite good condition after over six months. There is no doubt also that, although stock may not readily take to palm kernel cake at first, they will eat it quite well if it is not allowed to become stale in the feeding troughs, if it is not fed in too large quantities, and if it is judiciously fed and mixed with other foods.

ON THE RATES OF SOLUTION OF METALS IN FERRIC SALTS AND IN CHROMIC ACID.*

By R. G. VAN NAME and D. U. HILL.

(Continued from p. 21.)

Discussion of Results obtained with Ferric Salts.

TABLE VIII. contains a summary of the results given in the previous tables, each velocity constant being the averaged result of the various experiments performed under the conditions specified. These values have been obtained by one or the other of the two following methods—(a) For groups of comparable experiments in which the results were normal they are the averages, for all members of the group, of the average reaction velocity in each single experiment. (b) For groups of experiments in which the constants showed an unmistakable trend upward or downward they are the averages of the initial velocities as found by linear extrapolation. Although where method (b) is used the constants so calculated must be given the preference as more truly representative, the values calculated by method (a) are placed beside them, enclosed in parentheses, for comparison.

Considering first the upper section of the table, containing the ferric sulphate constants, we observe that in the presence of 5 molar sulphuric acid 5 metals give practically the same velocity, which, from the point of view of the diffusion theory, would be interpreted to mean that here the rate of diffusion of the ferric sulphate is determining the velocity. With decreasing acidity, however, the agreement becomes poorer, the metals tending to draw apart and to show individual velocities whose order is that of the electro-motive series, the more positive metal dissolving more rapidly. It is evident here that the specific nature of the metal has a distinct influence on the reaction velocity.

Such results as these are seemingly in direct contradiction to Nernst's hypothesis of infinitely high reaction velocity at the boundary surface between two phases. Nernst's hypothesis, as we have already seen, demands that in all normal cases, that is, in all cases not affected by secondary disturbing influences, the observed reaction velocity shall be determined by the rate of diffusion of the active substance, and shall be practically independent of the nature of the solid. Now it cannot be denied that disturbing influences may have slightly affected some of the results in the table; in particular, the nickel constants are rather uncertain. On the other hand, there was no

evidence whatever of interfering effects in the cadmium experiments. Moreover, the distinctly systematic nature of the results in the table argues against the possibility that any considerable number of them represent "anomalous" cases. Finally, the decreasing constants obtained with silver were clearly traced to the retardation of the chemical reaction by the accumulation of silver sulphate, which would have only a trifling effect on the rate of diffusion. In short, these results furnish grounds for seriously doubting the general validity of Nernst's hypothesis.

A study of the table seems to show that at one extreme we have velocities determined largely or wholly by diffusion, at the other velocities determined chiefly by the rate of the chemical reaction, and between them velocities in which we can readily detect the simultaneous effect of both influences. Although these results do not cover the full range from a purely chemical reaction velocity to a pure diffusion velocity it is evident that the transition from one to the other is gradual, not abrupt.

This point becomes clearer on further analysis of the results. An increase in the concentration of free sulphuric acid above 0.25 molar produces in all cases a marked decrease in the observed reaction velocity. In general, the activity of an oxidising agent is increased by a rise in the concentration of hydrogen ion. It will hardly be doubted that this rule applies in the cases with which we are dealing, and we should therefore expect that the free energy of the reaction with the metal would increase with increasing acidity. This is supported by the potentials in Table VI. so far as inferences can safely be drawn from the behaviour of electrodes which are imperfectly reversible. This table contains the single potentials of silver, copper, and cadmium against solutions of the same composition as those used in the reaction velocity measurements. As we have already noted, the values show that with increasing concentration of sulphuric acid the metal in all cases becomes less positive or more negative toward the solution; that is, the change is in the direction of increasing free energy.

TABLE VIII.—Summary of Velocity Constants.

	Molar concentration, H ₂ SO ₄ .			
	0.01.	0.5.	1.25	5.
<i>Ferric Alum.</i>				
Zinc ..	4.38	—	—	—
Cadmium	4.12	4.15	3.54	1.76
Iron ..	3.95 (3.82)	3.92	3.37	1.74
Nickel ..	3.80 (3.41)	3.75 (3.39)	3.27 (2.99)	1.71 (1.55)
Tin ..	—	3.60 (4.16)	—	1.72
Copper ..	—	3.74 (3.61)	3.30 (3.22)	1.71 (1.63)
Silver ..	—	1.67 (1.39)	1.63 (1.36)	1.24 (1.11)
<i>Ferric Chloride.</i>				
	Molar concentration of HCl.			
	0.1.	0.5.		
Cadmium	4.19	4.17		
Iron ..	4.14	4.35		
Copper ..	3.44 (3.22)	4.20 (4.30)		

For our purpose, however, the important question is the effect of an increase in acidity upon the velocity of the chemical part of the reaction with the metal. Although, in general, there is no necessary correspondence, even in sign, between variations in reaction velocity and variations in the magnitude of the change in free energy, there would seem to be here a rather strong probability that the chemical reaction in most or all of the cases with which we shall have to deal is accelerated rather than retarded by an increase in acidity. At all events we shall make this assumption as a working hypothesis, and shall adhere to it consistently throughout.

We must assume, then, that sulphuric acid tends to

* From the *American Journal of Science* xlii., 301.

accelerate the chemical reaction with the metal, but we find in Table VIII. that if the acid is present in more than 0.25 molar concentration it exerts a strong retarding influence on the rate of solution. From the standpoint of the diffusion theory the explanation of this effect is clear. The important factor here is the viscosity of the solution, which is increased in the ratio of about 2.5:1 when the sulphuric acid concentration rises from 0.25 molar to 5 molar. An increase in the viscosity retards the diffusion process by lowering the rate of diffusion, and, perhaps, to a slight extent, by increasing the thickness of the diffusion layer (see Van Name and Hill, *Am. Journ. Sci.*, xxxvi., 552), and in this way depresses the rate of solution of the metal, this effect here outweighing any acceleration of the chemical part of the reaction resulting from the higher acidity.

A predominance of the diffusion effect, however, does not necessarily exclude the influence of the chemical reaction, for we find that velocity constants in the same vertical column (that for 0.25 molar sulphuric acid, for instance), though they differ among themselves in a comparatively systematic manner according to the specific nature of the metal, thus showing the influence of the chemical reaction velocity, are all lowered by an increase in the viscosity. In other words, these results illustrate the case alluded to above, of a reaction velocity determined by the simultaneous influence and mutual relation of both factors, diffusion process and chemical reaction.

Nor is there any reason for believing that such cases are unusual. On the contrary, it seems proper to regard the observed velocity as being normally the resultant of the simultaneous action of the two factors just mentioned. Cases in which one factor predominates to the virtual exclusion of the other are, therefore, merely limiting cases, though no doubt they occur very often in practice.

This point of view appears to us to be the most reasonable and helpful one in dealing with heterogeneous reactions of the general type under consideration, and will be the one employed throughout the present paper in interpreting experimental results.

The results obtained with ferric chloride, summarised in the lower section of Table VIII., tend to confirm, so far as their evidence goes, the conclusions drawn above from the experiments with ferric sulphate. These values are probably less accurate than those for sulphate solutions, and less stress can be laid upon small differences. They prove that cadmium and iron dissolve in ferric chloride at the same rate in the presence of 0.1 molar hydrochloric acid, and probably also when the acid is 0.5 molar. This indicates that in these cases the observed reaction velocities are essentially rates of diffusion. It is not clear whether the effect of this increase in acidity is to raise or to lower the observed velocity, but the change is at all events small, as would be expected in a case in which the viscosity change is almost negligible (about 3 per cent.).

(NOTE.—In a like manner, the fact that the ferric sulphate constants change so little between 0.01 and 0.25 molar sulphuric acid, may be ascribed largely to the smallness of the accompanying viscosity change).

The same increase in acidity produces a marked rise in the rate of solution of copper. We would avoid laying any emphasis on the absolute values of these copper constants, on account of the complications already mentioned. Nevertheless, it may be pointed out that the relations of these two velocities to one another, and to the corresponding values for cadmium and iron, involves nothing unexpected or inconsistent with the point of view stated above. The lower value for copper in 0.1 molar hydrochloric acid, as compared with cadmium and iron, seems to be due to the influence of the relatively slower rate, in the case of copper, of the chemical part of the reaction, this rate being accelerated by the increase in acidity to 0.5 molar, up to the point where the rate of diffusion predominates, thus tending to bring copper into agreement with the other two metals.

To be continued).

REPORT OF THE CHEMIST,
DEPARTMENT OF AGRICULTURE, BUREAU OF
CHEMISTRY, WASHINGTON, D.C., U.S.A.

October 14, 1916

SIR,—I submit herewith the report of the work of the Bureau of Chemistry for the fiscal year ended June 30, 1916.—Respectfully,

C. L. ALSBERG, Chief of Bureau.

Hon. D. F. HOUSTON, Secretary of Agriculture.

There was marked advancement during the year in the work of the Bureau of Chemistry, both in the development of agricultural chemistry and the administration of the Federal food and drugs act. More than fifty scientific investigations were completed. The results have either been published or are in the process of publication. Among them may be mentioned the discovery of a new sugar, studies on the moulds and bacteria found normally in foods or producing spoilage in them, investigations upon torage and ptomaine poisoning, upon the physiological action of coal-tar dyes, upon vitamins, upon saponins, and upon the proteins of peanut, of kafir, and other seeds.

A large number of cases involving violations of the food and drugs act have been sent to prosecution. The number of civil and criminal actions recommended, however, is not a complete index of the success attained in securing protection for the consumer under this law. Manufacturers of food and drugs, more and more, are showing a willingness to comply with the regulations, and in many cases have improved their products so as to anticipate expected requirements. To such manufacturers the service and regulatory announcements have been of direct assistance. In these announcements manufacturers and others concerned with the operations of the food and drugs act obtain ample notice of the department's opinions with regard to various trade practices and through this, as well as through other channels, are notified promptly of all changes. These announcements are supplemented by publication of the results of investigations which have developed improved methods of producing foods and drugs. The producers and manufacturers of food products also have been assisted directly through practical demonstrations of better methods of preparing and conserving foodstuffs.

The development of methods for preventing avoidable waste and spoilage of food products and the devising of new and valuable by-products have had special attention with the object of relieving as far as possible the prices paid by the consumer for finished products by the elimination of losses and waste.

Special emphasis has been given by those in charge of the regulatory work in the past year to the control of drug products and in safeguarding the public from food subject to spoilage or pollution. Such foods if contaminated or improperly handled are liable to produce infection or poisoning and thus constitute a serious menace to health. With the object, therefore, of making the food and drugs act a hygienic measure as well as a preventer of economic fraud, the bureau has given especial attention to the interstate traffic in unclean milk, spoiled eggs, polluted oysters, and spoiled canned goods.

The interruption of imports has made it particularly important to the health of the people to curb the traffic in spurious synthetic drugs, because exceptionally high prices have offered unusual temptation to the sophisticator. Rigid enforcement of the Sherley amendment aimed at the false and fraudulent labelling of medicines was continued as a measure necessary for health protection.

As is pointed out in the report, much of the success in enforcing the food and drugs act has been due to the

effective co operation developed between State food, drug, and dairy officials and the Federal regulatory force.

Research.

Plant Chemistry.—Investigation of the nitrogenous compounds of kafir, *Andropogon sorghum*, has shown that fully one-half of them are soluble in hot 70 per cent alcohol. The soluble nitrogen consists in great part of a new alcohol-soluble protein, the percentage composition of which has been determined. It contains the amino acids lysin and tryptophan, both indispensable to the nutrition of animals. These are not found in zein, the corresponding protein of maize. Now that this is known a rational attempt can be made to learn how kafir may be fed to make it no less valuable than maize.

The peanut, *Arachis hypogaea*, and two globulins which have been separated from it have been found to contain an abundance of di-amino nitrogen. This form of nitrogen is indispensable to the nutrition of animals and is contained in inadequate amounts in the common cereals from which most feeds are derived. Peanut press cake should, therefore, prove to be an easily accessible material to make such cereal foods more efficient. In co-operation with the Bureau of Animal Industry it is planned to make a practical test of this matter.

From the jack bean, *Canavalia ensiformis*, two globulins and an albumen have been separated and studied.

The nitrogen distribution in cotton and tomato seed, cowpeas, corn, corn germ, and wheat has been determined.

Many analyses of forage plants of the arid and semi-arid West were made for the Bureau of Plant Industry.

New saponins have been isolated from *Yucca angustifolia*, *Yucca radiosa*, *Yucca filamentosa*, and *Agave lecheguilla*. A comparison of the surface-tension effect of a series of saponins with their hæmolytic power failed to disclose any inter-relation of the two properties of the saponins.

The glucoside in the leaves of upland cotton has been found to be quercimeritrin. The results of this work are in preparation for publication. The volatile oil distilled from the flowers has proven attractive to the boll weevil.

The results of the study of cyanogenesis in the common grass, *Tridens flavus*, showing that during maceration cyanogen may disappear, have been published. This observation signifies that many of the physiological studies upon cyanogenesis need revision.

The study upon boron absorption by plants discussed in the report for the year 1915 has been published.

A phytochemical laboratory has been established. It will undertake chemical investigations of the proximate principles of those plants which are of especial importance in connection with the enforcement of the foods and drugs act.

Carbohydrates.—A new sugar, the only heptose hitherto discovered in nature, *d*-manno-ketoheptose, has been separated from the avocado. The data are ready for publication. A large number of investigations upon the preparation, the mutarotation, and the rotatory power of sugars and sugar derivatives have been completed and prepared for publication. Some of the results were published during the year in the following papers:—"The Acetyl Derivatives of the Sugars"; "The Isomeric Pentacetates of Glucosamine and Chondrosamine"; "The Isomeric Tetracetates of Xylose and Observations Regarding the Acetates of Melibiose, Trehalose, and Sucrose"; "A Fourth Crystalline Pentacetate of Xylose and Some Related Compounds"; "A Second Crystalline *d*-Fructose Pentacetate"; "Crystalline β -Methyl Fructoside and its Tetracetates"; "The Preparation of Melibiose"; "Bromoacetyl Xylose and β -Triacetyl-methylxyloside."

Papers have been published upon the occurrence of sucrose in relatively large amounts in a new seedling grape and upon the occurrence of sucrose in grapes of American origin. *Bulletin* No. 335, entitled "Develop-

ment of Sugar and Acid in Grapes During Ripening," has been issued.

Flora of Foodstuffs.—An investigation of the range of conditions under which organisms of the *Bacillus botulinus* group may cause sickness or death in human beings and in domestic animals has been started. It was found that a strain of this organism obtained from a food poisoning case produced a very powerful poison. In co-operation with the Bureau of Animal Industry this poison was shown to affect rabbits, donkeys, and horses very quickly, cats in some cases and not in others, and not to affect fowls.

Because the losses to individual packers of sardines from swelled cans may be as high as 30 per cent of the yearly pack, this form of spoilage has been studied in the hope that means for preventing this waste may be found. The organism causing spoilage very rapidly forms spores which are killed only at high temperatures. Therefore, aside from ordinary cleanliness, careful processing at high temperatures is necessary to prevent the subsequent swelling of cans. In the "red feed" within the stomachs of "belly-blown" sardines a gas-producing bacterium, pathogenic to guinea pigs, has been found. A spore-bearing, gas-producing anaerobe identical with that found in sardines was isolated from two different consignments of spoiled sweetened condensed milk. *B. mesentericus ruber* was found to be the cause of the rose-pink colour of certain spoiled sweetened condensed milks.

A general comparative study of the mould flora of the food-stuffs subjected to inspection has been begun, carefully distinguishing accidental organisms present as resting spores and those active in producing changes in the substrata.

The study of the effect of storage on bottled waters has shown that *B. coli*, *B. typhosus*, and *B. dysenteriae* inoculated into bottled mineral waters do not multiply, except the first two, which, in some instances, increased slightly during the first two days of storage. This was followed by a decrease in numbers. In a water practically free from dissolved solids, *B. coli* persisted in greatly reduced numbers for more than six months. A yellow micrococcus, multiplying rapidly, was found to be due to air contamination. The manner in which commercially bottled water changes its flora in one to six months was studied in considerable detail. *Bulletin* No. 369, "Bacteria in Commercial Bottled Waters," was issued. The results of a comparison of bile with lactose buillon for determining the presence of *B. coli* in water were also published.

The United States Public Health Service has been assisted by the Bureau of Chemistry in making sanitary surveys of oyster beds. The results of a study of the preparation for and the transportation to the market of oysters, of a comparative study of bacteriological methods for the examination of oysters, and of a comparative bacteriological examination of oyster-shell liquor and oyster meats have been prepared for publication.

In co-operation with the Bureau of Animal Industry a manuscript has been prepared showing that one member of the group of moulds known as *Aspergillus niger* produces ten times as much oxalic acid as others, without accompanying differences in structure.

It has been found that the common moulds *Penicillium camemberti* and *Aspergillus niger* produce substances reacting with ferric chloride like phenols, a matter of significance in detecting mouldiness in foods. It has also been found that the so-called salicylic acid reaction of the Japanese distilled liquor, sake, is in reality due to an acid formed by the mould used to ferment the rice from which sake is distilled. Mould products of this type may be mistaken for preservatives such as salicylic acid.

An as yet undetermined species of ergot was discovered in caraway seed.

Anti-neuritic Substances.—A variety of synthetic compounds have been made and tested physiologically. Several have been found to possess anti-neuritic properties similar to natural "vitamines." In collaboration with the

United States Public Health Service a crystalline anti-neuritic product was isolated from yeast and some evidence obtained regarding its identity. A study of the nutritive and medicinal value of cod-liver oil and extracts thereof was begun. One paper has been published and three nearly completed.

Cereals, Flour.—Studies have been made upon the grading of flour and upon the determination of grades of flour with especial reference to the bleaching of flour. It has been found that the particles of various sizes in flour differ in chemical composition and in baking qualities. The work on flour substitutes has been continued, and a report on the determination of moisture in bread has been made. Chemical studies have been made upon the changes that take place in the deterioration of oats and in the bleaching of inferior oats. Studies upon rice milling by-products have been completed. *Bulletin* No. 330, "The Milling of Rice and its Mechanical and Chemical Effect on the Grain," has been issued jointly with the Bureau of Plant Industry.

Spices.—Studies have been made of pepper, mustard, celery, caraway, and poppy seed, savory and sage leaves, and saffron to determine their constants as a guide in regulatory work. The determination of oxalic acid in pepper and cinnamon has led to a revision of the statements in the literature on this subject. Gingerol, the pungent principal of ginger, an oily liquid boiling at 227—229° C. at 6 mm. pressure, and paradol, isolated from grains of paradise, have been studied.

Fats and Oils.—In co-operation with the Bureau of Plant Industry a bulletin has been issued upon peanut oil. A paper has been issued upon American charlock oil.

Drugs and Pharmacology.—Papers have been published on "The Stability of Nitrous Ether" and on the "Periodides of Paenacetin, Methacetin, and Triphenine." The results of investigations upon the "Periodides of Antipyrin, Iodantipyrin, Pyramidon" have been completed for publication.

Studies upon the heavy metals that may contaminate foods have been continued, and some of the results published under the title "The Influence of Heavy Metals on the Intestines." Papers upon the action of citrate and its decomposition in the body and upon the elimination of malate have been prepared for publication. An article on the toxicity of a series of oil soluble dyes in which it is shown that some of them are eliminated in the urine combined with glycuronic acid has been finished and will soon be published. As a by-product of the study of the toxicity of water-soluble dyes containing iodine in the molecule, a research upon the influence of iodine and sodium iodide on the circulation has been printed. It has been found that digitalis and adrenalin antagonise the toxic heart action of oil of chenopodium while caffeine is synergistic. The result of this investigation has been published.

Insecticides and Fungicides.—A tree-banding material has been developed, which has been used by the Bureau of Entomology in its gipsy moth campaign. It promises to prove superior to, and cheaper than, the materials now in use in this country.

The Federal Horticultural Board has been further assisted in the fumigation of cotton bales, and the process has been so improved that a large part of the hydrocyanic acid used is recovered. One of the largest plants is now operating by this method.

In co-operation with the Bureau of Plant Industry attempts are being made to so modify the formula for Bordeaux mixture as to render it more efficient, while at the same time reducing the amount of copper therein.

A paper upon the reduction of As^{+5} to As^{+3} by cuprous chloride and the determination of arsenic by distillation as arsenic trichloride has been published, while others upon "The Preparation and Properties of Lead Chlor-arsenate—Artificial Mimetite" and "The Arsenates of Lead" are in press.

Analytical Methods.—Methods for the estimation of

volatile esters in citrous oils and extract, of alcohol in the presence of phenol, of phenacetine and salol in admixture, of tartaric acid, and of raffinose by enzymatic hydrolysis, have been published.

The results of investigations upon the identification and determination of lactic acid in biological products, upon the separation of lithium from the other alkali metals, upon a study of the Kjeldahl method for determining nitrogen, upon the freezing-point of milk as a means of detecting water, upon the detection of watered milk by means of simplified molecular concentration constants, upon the detection of ergot and moulds in food and drug products, upon the determination of the quality of gelatin by the measurement of its mutarotation, and upon the quality of commercial litmus papers have been prepared for publication. A method has been devised for distinguishing between bottle fermented and artificially carbonated wines.

The collation of the mass of information upon methods of food and drug analysis accumulated by the Bureau described in the report for 1915 has made great progress. Forty-five subjects were finished during the year, making 66 in all since the work was begun. Much of the work is more than compilation, since the aim is to present the Bureau's collective experience during the past fifteen years. This requires not merely the critical sifting of the Bureau's records, together with a study of the literature, but also not infrequently independent research.

Conservation of Foodstuffs.

Poultry, Eggs.—A precooling plant has been developed, cooled by ice, capable of chilling 15 000 lbs. of eggs and poultry a week, costing, installed, approximately 800 dols. With ice at 3 dols. per ton it has been found in actual commercial use to effect a saving of at least 22 dols. per carload in handling and chilling. The project upon improving the methods of fleshing poultry for the market has been continued. The work upon the transportation of perishables has been facilitated by the improvement of the method of installing resistance thermometers in refrigerator cars so that the temperature of the interior of a considerable number of cars may be observed simultaneously. The results of the previous work on damage to eggs in transit are being seen plainly throughout the country in greatly lessened waste at destination. Reports for the metropolitan district of New York City indicate that 41,161 dozens arrived broken during the calendar year 1915, while approximately twice that number were broken on arrival during 1914. In the study of the cold storage of eggs particular attention has been paid to the devising of methods to prevent stored eggs from acquiring the so-called "storage" taste. *Bulletin* No. 224, "A Study of the Preparation of Frozen and Dried Eggs in the Producing Section," has been issued.

An investigation has been made of the contents of the crop of fowls for the purpose of furnishing data to detect the feeding, as a makeweight, of excessive quantities of sand just before slaughtering.

Fish.—Demonstrations in the preparation of fresh shrimp for the market with cleanliness, suitable boiling in brine, and thorough cooling has been of material value to the shrimp shippers of the southern east coast in the conduct of their business.

Studies of fish transportation to prevent decay have been continued. Perhaps no other perishable food is shipped long distances with so little knowledge of what is required to insure arrival in good order. The work was begun in Florida, and at the end of the shipping season transferred to the Pacific coast, where transcontinental hauls are under observation. A Yearbook article upon the fish industry was published. Many analyses of food fish have been made which show that the data now on record are inaccurate because, as a rule, they were made without consideration of the season when the fish were taken. The studies upon the chemical changes taking place in fish in freezer storage begun last year has been continued.

The investigation upon the improvement of the methods of canning sardines has been brought to a successful conclusion. The industry has very largely accepted the recommendations of the Bureau. It has taken steps to see that only sound fish are packed by imposing upon itself an inspection service.

Potatoes.—A process has been perfected for the drying of surplus and cull potatoes with simple machinery for the purpose of utilising these tubers now largely wasted in certain localities in years of over production. The product can be fed to animals or be used as a size, or for the manufacture of gum, dextrin, or starch. Being dry, it can be stored indefinitely, and transported more cheaply than the potato itself.

A simple practical method of ensiling potatoes without cooking or the use of pure cultures has been discovered. To the crushed raw potatoes is added a starter consisting of 1.5 to 4 per cent of ordinary corn meal. The loss from the resulting fermentation is negligible. Cattle and hog-eat the product freely. Extensive feeding experiments are planned for the coming year.

Citrus and other Fruits.—The development of a method for the manufacture of citrate of lime from lemons has been completed, while the development of a method for the manufacture of citric acid free from contamination by heavy metals is well advanced. The manufacture of lemon oil has been further studied, and the determination of the seasonal variations of the oil and citric acid content of lemons has been practically completed for certain sections of California. A study of tangerines has shown that the green fruit has value as a source of citric acid, and that the oil has commercial possibilities. The manufacture of marmalade stock has been undertaken. A fine orange vinegar has been manufactured on a small commercial scale which promises to find a market, though a limited one, because it costs more to produce than the usual product. The determination of the composition of California oranges with reference to season, climate, soil, location, and methods of cultivation has been completed, and the results are being prepared for publication. The study of the composition of oranges from selected trees has been of great assistance to the Bureau of Plant Industry in studying bud variations for the purpose of making selections in propagation experiments. Similar studies upon grape fruit have been begun with the Bureau of Plant Industry for the purpose of standardising and improving the varieties grown. A study to establish the range of variation in composition of mature Florida and California grape fruit has been undertaken to be carried through several seasons.

Improved methods for the preparation of jams and jellies have been devised, and manufacturers have been assisted in improving their methods and utilising their waste products. In connection with the States Relations Service, from time to time lectures and demonstrations have been given at meetings of State agents upon the methods of preparing jams, jellies, and preserves in the household.

Miscellaneous.—A method has been developed, though not yet applied on a large scale, by which a pure cane syrup can be made which will not crystallise nor ferment. The studies upon the effect of the different manufacturing processes upon the composition of maple syrup and of sorghum syrup have been continued. A paper has been published upon the composition of tamarind syrup.

Beans produced in certain localities are not as highly esteemed as their otherwise excellent quality warrants, because when soaked they do not swell uniformly. It was found that a cuticular substance is especially abundant in the epidermis of the hilum of those beans which, when soaked, swell slowly. The oxalic acid content of a large variety of beans has been investigated.

An investigation of the sauerkraut industry has shown that while factory construction and management have largely followed German models, the climatic differences between this country and Germany have not been con-

sidered. Adequate temperature controls to diminish losses in waste liquor, kraut, and brine have not been provided.

Technological Investigations.

Dust Explosions.—For the prevention of explosions in the threshing of grain an automatic fire extinguisher, a blower device, and a plan of wiring the machines have been devised in co-operation with the Office of Public Roads and the Bureau of Mines. They were described in a joint bulletin with the Office of Public Roads, *Bulletin* No. 379, and blue prints were furnished to all manufacturers of threshing machines in the United States by that office. Detailed information has also been sent to underwriters and to farmers' mutual insurance companies dealing in threshing-machine insurance. Plans were made jointly with the Office of Public Roads to demonstrate these devices in the field, with the assistance of the State experiment stations of Idaho, Oregon, and Washington. The States of New York and Pennsylvania have been assisted in the drafting of regulations designed to reduce the danger from dust explosions and fire in mills and elevators. With the assistance of the Bureau of Standards laboratory apparatus was constructed for the mechanical separation of dust into fractions of definite size and density. By means of specially designed apparatus the force developed by the explosion of various kinds of dust has been measured. Results of the investigation upon the inflammability of carbonaceous dusts and upon the inflammability of carbonaceous dusts in atmospheres of low oxygen tension have been prepared for publication. In co-operation with the State College of Pennsylvania, the study of explosions in attrition mills has been begun.

Paper.—A test has been found to determine the strength of paper when wet, which is a most important consideration in preparing specifications for photographic blue and brown print, bag, and wrapping papers. An instrument has been constructed for the measurement of the trans-ucency of paper. Instructions for testing the folding endurance tester, with data on the accuracy of this machine, have been prepared for publication. Papers have been published upon a new colorimeter and upon the detection of faulty sizing in high-grade papers.

Tanning.—A manuscript has been prepared upon American sumac to aid the farmer in gathering this plant and to help supply the demand in the dyeing and tanning industry. It has been found that the best way to denature egg yolk for tanning is to add 2 per cent of birch tar oil. Power distillate may also be used.

Naval Stores.—The Board of Trade of Brunswick, Ga., adopted the glass standards of the rosin types. They are now practically universally recognised in the Union. Examination of samples of rosin, mostly the pale grades, representing nearly 6000 barrels, showed 9 per cent to have been graded too low and 38 per cent too high. A method for defining and determining the grades of turpentine has been perfected. A rough survey was made east of the Mississippi to determine the extent of the adulteration of spirits of turpentine sold for technical purposes. Twenty-six per cent of the samples were found to be adulterated with mineral oil to the extent of from 3 to 100 per cent.

Demonstration.

In connection with its research and regulatory work the Bureau has done much demonstration and educational work. This has during the past years grown to such an extent that it deserves separate notice. Some of it has already been mentioned, as, for example, that in connection with the canning of sardines, the manufacture of dried and frozen eggs, the refrigeration of perishables, the shipping of fresh shrimp, and of fresh fish. The work of the poultry and egg packing demonstration car has increased greatly in efficiency and results. During the year 101 towns in the State of Indiana were visited, and 10,600 people came to the car.

An extensive demonstration campaign has been con-

ducted on the proper methods of packing tomato products, which supplements the effect of prosecutions in eliminating unfit products from the market. In co-operation with the States Relations Service, assistance has been given to canning clubs, especially in Florida, in the preparation of jams, jellies, and preserves. Assistance has also been given to manufacturers of these products. Instruction has been given in the grading of naval stores. Unfortunately a sufficient number of glass standards is not yet available, because the disturbed trade conditions make it impossible to secure the necessary glasses. The demonstration of improved methods of producing rosin and turpentine has been begun in a small way. It is soon to be made more extensive.

(To be continued).

PROCEEDINGS OF SOCIETIES.

SOCIETY OF CHEMICAL INDUSTRY. (LONDON SECTION).

Ordinary Meeting, December 4, 1916.

Mr. ARTHUR R. LING in the Chair.

In the absence of the authors, Mr. J. A. REAVELL read a paper, of which the following is an abstract:—

"Production of Nitrate of Soda in Chile, Past, Present, and Future." By I. BIRKWOOD HOBBSBAUM, A.M.S.T., F.C.S., and J. L. GRIGIONI.

A survey was given of the nitrate industry from its birth in 1809, when the most elementary apparatus was in use and only the richest of material was extracted, namely, that containing 60 per cent of nitrate, followed by a period of trial and experiment in the use of evaporation by coils and pipes, until in 1832 the first well-considered plant was put down by Sir Robert Harvey, who incorporated on a large scale and in a well-considered scheme the results of all the past experience, including that of Mr. J. J. Humberston, to whom was due the present counter-current system of lixiviation of the raw material, which was universally in use at the present day in Chile. By means of that system, raw material could be economically worked with about 30 per cent nitrate content.

The authors pointed out that that plant, erected in 1884, produced about 6000 tons of nitrate of soda per month, and for every ton of coal burnt 12 tons of nitrate of soda were manufactured. So stationary was the industry from that time onwards that in 1914, thirty years later, there had been no improvement in the production, with the exception of mechanical labour saving devices, such as elevators. These improvements, made between 1900 and 1915, were illustrated by a detailed account of one of the latest works designed in 1911, for a monthly output of 90,000 quintals, but an examination of the working figures showed that the tons of nitrate produced per ton of coal had fallen from 12 to 1, to 5.3 to 1. This, however, was due to the fact that in this later plant caliche of a much lower grade was being used; a nitrate which could not have been treated at all by the plant erected in 1884.

The authors then gave very full details of the actual crushing and leaching systems now in use for obtaining the nitrate of soda solutions, and showed wherein these systems were unsatisfactory, and pointed out the real causes of their inefficiency. Following this was an outline of various attempts—more or less spasmodic and unorganised—to improve the present system: attempts which had all broken down from the fact that they were not of a sufficiently radical nature, but simply attempts to palliate existing evils in the present plant.

Two processes were described which had been extensively worked out and tested by continuous experiments

and sustained research until they could now be looked upon as practical propositions, namely, the "Butters" process and the "Gibbs" process.

The "Butters" process used ball mills for crushing the raw material in the presence of hot, weak nitrate solution. This was then treated in the well-known Butters patent vacuum filter, which had been applied on a very large scale at one of the offices, and proved very successful. The criticism of the process was that it did not go far enough, as it was not definitely connected with any evaporation process, a deficiency which the "Gibbs" process had overcome by the adoption of the Kestner patent salting evaporator, in place of the primitive types of evaporator hitherto tried in conjunction with the Butters system.

In 1912, the authors made a tour of investigation for Messrs. Gibbs and Co., of Valparaiso, throughout the U.S.A., France, and Germany, in order to gather information on methods used in other industries so as to develop the Chilean nitrate industry on more modern lines. That resulted in a process combining a new method of lixiviation, also a new method of concentrating the liquors so produced in Kestner evaporators, including the separation of the sodium chloride and nitrate of soda.

The theoretical details of the problem and the details of the lixiviation process were worked out partly at the Manchester School of Technology and at the laboratories of Messrs. G. T. Holloway; whilst the evaporator problem was solved by Mr. Paul Kestner, of Lille, who acted in conjunction with the Kestner Evaporator and Engineering Co., Ltd., and the authors of the paper.

The principles of the Gibbs process were as follows:—The raw material was first crushed and fed into a disintegrating mill, working without balls or pebbles, together with nitrate solution at about 15° C. In that mill the raw material was reduced to its ultimate particles with the minimum of grinding. The solid mass was fed continuously from the mill to a series of classifiers in which lixiviation again took place on the well-known counter-current system. The action took place in four stages and the final insolubles were in the form of clean sand and gravel, which did not contain any more than $\frac{1}{2}$ per cent of nitrate of soda. In order to eliminate the very fine insolubles, about 10 per cent of the raw material was treated in a filtration process—in an Oliver filter. The result was to produce a liquor containing about 450 grms. of nitrate of soda per litre and about 200 grms. of salt with 50 to 60 grms. of other soluble salts. The liquor so produced was carried to the Kestner patent salting type evaporator. This consisted really of three evaporator units; the first two worked in double effect and the last unit worked independently under vacuum.

The special feature of these evaporators was the arrangement of a central separator surrounded by several calandrias placed tangentially. These calandrias, or heating units, were so connected to the central separator that a constant circulation of liquor took place through the evaporation tubes, whilst the salts thrown out of solution as concentration proceeded were trapped and carried to the bottom of the separator, so that they did not again enter into circulation. Further, each calandria could be isolated from the separator and independently washed—a highly important feature when dealing with caliche liquors which contained, in addition to nitrates and chlorides, quite appreciable quantities of other soluble salts as well as slime and mud. In the first evaporator unit, the weak liquors coming from the ball mills were pre-concentrated, so as to prepare for the second effect a liquor of uniform density. That evaporator was operated by the vapours driven off in evaporator No. 2, where the final concentration of the liquors was carried out. In the second evaporator, the liquor in the separator was kept at a pre-arranged maximum boiling point at which all the sodium chloride was thrown out of solution, and removed in a special filter-box, while the highly-saturated nitrate liquor was carried into a third effect. In this third effect further

evaporation might take place, or depending on the operation in the first part of the process, the final stage might consist only of self-evaporation and cooling in vacuo, with the consequent throwing down of crystals of nitrate of soda.

The authors refuted the statement so often made that the nitrate grounds of Chile were practically exhausted, or would be so within a few years. According to the official returns, there was sufficient supply to last for at least one hundred more years. There was, in fact, according to the authorities in Chile, 245,300,000 tons of nitrate awaiting treatment by some economical process.

DISCUSSION.

The CHAIRMAN complimented the authors on the interesting character of their paper. He said it was a remarkable fact that the nitrate industry had only recently commenced to use multiple-effect evaporators.

Mr. W. G. MANN referred to the paucity of published literature on the subject. In regard to atmospheric cooling and crystallising in open tanks, there were in connection with every oficina some hundreds of open cooling tanks which ought to offer opportunities for very reliable data on the subject. In the new system of nitrate production, the problem of quick and efficient cooling and crystallising was very important. He suggested that some of the fundamental problems of chemical engineering might be investigated by a committee of the society. With regard to the expressions of surprise made by the chairman and others that the multiple-effect evaporators had not been in use on caliche, he drew attention to the difficult nature of the caliche liquor from the point of view of the evaporator problem. The trouble was further aggravated by the presence of fine dust from the crushing mills. It had been solved by the introduction of an evaporator which allowed for rapid circulation in the heating tubes and the isolation and cleaning of the heating units by means of the multi calandria arrangement attached to a central separator.

Mr. E. V. EVANS said that it was often necessary to design a cooling system for hot saturated solutions of a crystallisable product, which, on cooling to normal temperature, set almost solid. The means suggested to overcome this difficulty were to employ a high speed centrifugal pump for pumping the hot liquor through a long coil of iron pipe, which was cooled externally by liquor. If the speed of the centrifugal pump was sufficiently high the tendency for the crystals formed within the liquor to cleave to the pipe was overcome by the high velocity of flow.

Dr. R. SELIGMAN said that it had been stated in the paper that crude oil was available for fuel purposes on the Caliche fields, but presumed that what was meant was that crude oil was more readily available than coal, and not that oil of local occurrence was used. He further asked whether on the Caliche fields water was not extremely scarce, and consequently valuable, and if that were so, it seemed all the more remarkable that methods of evaporation and drying were used which seemed especially designed to waste water rather than to conserve it.

Sir FREDERICK NATHAN said he could confirm the presence of iodine in Chile saltpetre, and he had often seen crystals of iodine subliming over with the nitric acid produced from Chile saltpetre.

Mr. WALTER F. REID expressed surprise that the iodine was not recovered as a by-product. It was very much required in the manufacture of organic chemicals. He would like to ask if the question of evaporating in open tanks by means of the sun had ever been dealt with in Chile.

Mr. J. W. MACDONALD said that if the Chilean fields were so close to exhaustion as some had asserted, why were they not more careful in recovering the whole of the nitrate? He thought that a diffusion process, similar to that used in the extraction of sugar from beet, might

probably replace the Gibbs system. Less water would be required.

Mr. T. D. MORSON said that the present price of iodine was altogether an artificial one, and agreed that it should be recovered.

Dr. MESSEL inquired how much iodine was available per ton of caliche.

Mr. REAVELL briefly replied to the discussion, and the meeting terminated with a vote of thanks to the authors.

Informal Meeting, December 19, 1916.

Mr. ARTHUR R. LING in the Chair.

The CHAIRMAN said that it was hoped that the present departure of holding informal meetings would prove useful in promoting the good fellowship of the members, as well as indicating new lines to be followed in increasing the utility of the Society's work. It was further hoped that the younger members might be induced to join more freely in the discussions than they had done heretofore.

There was a strong feeling among members, especially those in the provinces, in favour of the reporting of proceedings of the meetings other than papers and discussions, so that the different sections should become better acquainted with what each was doing. To some extent that was reported at the present time in the trade journals. But it was strongly urged, and he thought quite reasonably, that their own journal was the place where they ought to find a record of their doings.

He believed that the question of the Federation of Chemical Societies, as suggested by Prof. Armstrong in a paper read before their section last year, would be promoted to a great extent by holding meetings such as the present one. There was no doubt that the time had come when chemistry in this country must make its voice heard as medicine had done. It was a remarkable fact that when the Government or any corporate body wished for any assistance in chemistry, they did not approach the Society of Chemical Industry, which, it appeared to him, was the proper body to deal with such matters. He might cite the fact that at the outbreak of war, the Government approached the Royal Society, who formed various committees, to deal with chemical questions. If the various chemical societies had been federated, then a question such as that would have been submitted to them. It seemed to him that it was just as logical for the Government to go to the Royal Society on a medical question as it was for them to go to that society on a chemical question. The reason the medical profession had not been excluded was that they had made themselves known, and made themselves strong by federating.

In 1893, when he became Secretary of the London Section, the membership was about one thousand, and now it was slightly over that number, so in those eighteen years there had been no substantial increase. Surely, it should have been otherwise. He urged them to use their endeavours to induce their friends to join the Section.

DISCUSSION.

Mr. A. H. DEWAR welcomed the meeting as an indication of a move in the direction of making the Society more useful. He thought that they should aim at obtaining papers of a more technical nature, and he expressed the view that many of their papers belonged more to the domain of pure than applied science. He pointed out that some directors were afraid to let their chemists speak, but if wise use was made of intercourse between chemists it was conducive to their companies' advantage.

Dr. S. MIALL alluded to the difficulty felt by a manufacturer who was rather ignorant of chemistry. He found few papers which were sufficiently elementary and general to interest him, and hoped it would be possible to introduce more into the Journal. He called attention to the amount of space taken up by abstracts of highly

technical matters. Finally, he hoped the section would be able to arrange visits to works.

Mr. W. J. COWAN agreed with holding informal meetings of the kind. He thought that the Journal might be improved in its general interest to members if, amongst other things, it contained "Answers to Correspondents" on matters of general trade importance to chemical industry. He favoured the establishment of a club for chemists and others allied to chemical industry and chemical engineering, which he thought was a long felt want as the means of creating a closer *esprit de corps* among the members. He urged that the Council should take some action with the Government on the question of English patents granted to foreign manufacturers, many of which were worthless in their literal and printed form.

Mr. H. E. COLEY suggested that a small committee be formed immediately, consisting preferably of members not at present on the executive, which should draw up a scheme for the formation of a chemical club in connection with the society. He argued that the present form of monthly meeting was out of date. The impression in the mind of the ordinary member of the society was that nothing had been done to make for unity, and that something ought to be done quickly.

Dr. H. V. A. BRISCOE thought that the present time was one of great opportunity and yet of great difficulty. He would suggest that an immediate step might be taken to arrange at meetings, such as the present, discussions on set subjects selected by the committee. They might thus acquire the habit of "talking shop" judiciously, without revealing confidential information. With reference to the complaint made by one or two speakers that only a few pages of the Journal were of interest to them, he presumed that only one or two pages dealt with that branch of industry with which they were primarily concerned, and he would suggest to these gentlemen that they were taking too narrow a view of the matter, and that they might find it worth while to study the pages in which they were not interested in the narrower sense. He agreed entirely with Mr. Cowan that many foreign patents as specified were unworkable.

The HON. SECRETARY pointed out that as far back as April, 1914, he had proposed to the committee a resolution, which was agreed to unanimously:—

"That it was desirable in the interests of the Society to consider a scheme for the formation of a Chemical Club, with suitable premises in London."

For various reasons that scheme could not be proceeded with at that time, but he believed that there were now large numbers of the members of the London Section who would be willing to support actively the furtherance of this proposal.

Dr. C. A. KEANE expressed himself thoroughly in sympathy with the proposal that steps should be taken to effect some fuller opportunity than had existed in the past for the members of the section to meet together on a social basis and to get to know one another. In the past the committee of the section had done their best to advance what they regarded as the best interests of the members, but as with all committees and councils the ideas for such advancement necessarily came from within the circle of the committee itself, and they knew all too little of the views and desires of the bulk of the members of the section. This meeting had given opportunity for these views to be stated, and he felt sure that every member of the committee would appreciate the freedom with which members had spoken. It appeared to him to be quite within the powers of the section to take steps to initiate something in the form of a meeting place or club for social purposes, apart from the more formal gatherings for the reading of papers.

Mr. BERNARD F. HOWARD said that the meeting had amply justified itself, and it would be a matter of great regret if it were not reported. Many points had been raised that evening which could well form the basis for an

evening's discussion at an informal meeting, e.g., relation between chemists and directors, labour difficulties, &c.

Mr. HOWARD then proposed the following resolution, which was seconded by Dr. W. HODGKINSON, and carried:—

"That a committee be appointed to consider the steps that should be taken to form a chemical industry club for the London Section of the Society of Chemical Industry, and to report to the committee of the section, and, subsequently, to a further informal meeting of the members of the London Section."

The following members were appointed to form a committee:—Messrs. H. E. Coley, A. H. Dewar, B. F. Howard, with the Chairman and Hon. Secretary *ex officio*.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxliii, No. 20, November 13, 1916.

Colloidal Iodine.—H. Bordier and G. Rzy.—It has already been shown in a previous communication that solutions of iodine in water appear to contain the iodine in the colloidal state, but it is difficult to establish the fact by a cryoscopic method, as the quantity dissolved is too small for the purpose. Investigation with the ultramicroscope indicates that iodine is present in pure water in the colloidal state, but in the form of granules which are too small to be seen with the instrument. Gelatin in suitable proportions makes these granules unite to form particles which can be seen.

MISCELLANEOUS.

Special Reports on the Mineral Resources of Great Britain.—The Board of Agriculture and Fisheries desire to give notice of the publication of a second edition of the second volume of the Special Reports on the Mineral Resources of Great Britain, which has been prepared by the Director of the Geological Survey in response to numerous enquiries that have arisen through the conditions brought about by the war. In the main, it is a reprint of the first edition, wherein the uses, distribution, treatment, and output of Barytes and Witherite are dealt with, and particulars of the mines—active and inactive—are given. Copies may be obtained through any bookseller; from Messrs. T. Fisher Unwin, Ltd., 1, Adelphi Terrace, London, W.C., who are the sole wholesale agents to the trade outside the County of London; or from the Director-General, Ordnance Survey Office, Southampton. Price 2s.

Industrial Research in Leeds on German Dyes.—Among the industries affected by the cessation of supplies of German-made dyes are printing and photography. Modern colour-printing for illustration work is dependent on the use of photographic plates which have been specially rendered sensitive to red and other colours to which they would ordinarily be blind. It has also been found necessary to use such panchromatic plates for military photography in aeroplane reconnaissance work, on account of their superior powers of resolving detail and of penetrating fog or mist. For the manufacture of such plates certain special dyes were essential, and these were obtained solely from Germany. The quantities used are very small, and the stocks in this country sufficed to carry

on the manufacture for a considerable period after the outbreak of war. Some six months ago, however, the principal makers notified the trades concerned that the supply of such plates could not be guaranteed in the future. The Federation of Master Printers discussed the position at a meeting at which the Leeds Technical School was represented. The photographic and printing crafts' department of the school had previously had considerable experience in using and testing these dyes and undertook to assist in the solution of the difficulty. The University of Leeds was approached by the Leeds Education Committee, with a view to its co-operation in the preparation of the dyes used, and cordially agreed to a combined investigation. Without loss of time a joint scheme of research was organised by the two authorities, and the work was entrusted to Mr. W. Harrison, M.Sc., a member of the University staff, and to Mr. S. F. Bottomley, F.R.P.S., head of the printing crafts' department of the City of Leeds Technical School. Although the research is still in progress, it has already yielded important results, and on account of the urgency of the demand a preliminary report has been printed for the information of all concerned. This pamphlet gives full details of the preparation of two dyes, to which the names Formocyanine and Tolucyanine are given, and demonstrates that their sensitising powers are identical with those of the original German products. The work is being continued with the object of increasing the yields of the dyes already made and of preparing other dyes which are also required in the industries concerned.

Mineral Resources of the United States.—The Department of the Interior has recently issued a series of pamphlets dealing with this subject. Among the subjects of these pamphlets are the following:—Chromic iron ore, production of various metals, fuel briquetting, asbestos, fluorspar, felspar, silica, graphite, &c. The methods of production, commercial uses, and properties of the various substances are in each case discussed in some detail, and the distribution of the minerals throughout the different States is given in full. The variations of prices and quantities exported and imported are tabulated, and the progress of trade is shown by statistics and diagrams.

Commercial Nagoya.—The paper *Commercial Nagoya* is Nagoya's first and only periodical published in English, and aims at bringing Japanese business men into closer touch with foreign firms. The August, 1916, number contains some accounts of the industries of Nagoya, and reports that Japan's export trade is beginning to make great strides. Some articles, such as rubber goods, which before the war were imported from Germany, are now being manufactured in Japan, and machinery, beer, and other things are being exported for the first time. The periodical contains many advertisements of firms dealing in various different classes of goods, and deserves the attention of British merchants. It is published by the Aichiken Commercial Museum, Nagoya.

Announcement.—The Cambridge University Press will shortly publish "Comptes Rendus of Observation and Reasoning," by Dr. J. Y. Buchanan, F.R.S., chemist and physicist of the *Challenger* expedition. As the title indicates, the book consists of "accounts rendered" of work done at different times, in different places, and on different subjects. The following papers are included in the volume:—Recent Antarctic Exploration. Chemical and Physical Notes. On Ice and Brines. On Steam and Brines. The Size of the Ice-Grain in Glaciers. Ice and Its Natural History. Beobachtungen über die Einwirkung der Strahlung auf das Gletscheris. In and Around the Morteratsch Glacier: A Study in the Natural History of Ice. The Use of the Globe in the Study of Crystallography. On a Solar Calorimeter, used in Egypt at the Total Solar Eclipse in 1882. Solar Radiation. The Total Eclipse of August 30, 1905. Eclipse Predictions. The Solar Eclipse of April 17, 1912. The Publication of Scientific Papers. The Royal Society. Nomenclature

and Notation in Calorimetry. Thermometric Scales for Meteorological Use. The Metrical System. The Power of Great Britain, and the House of Commons. Lord Milner and Imperial Scholarships. And History in Handy Volumes. Of the scientific communications, the most important are those concerning the Natural History of Ice and Steam. The contributions to newspapers concerning matters of public interest at the time have been reprinted, because they are of public interest still. Dr. Buchanan's earlier volume of scientific papers (Oceanographical) will be remembered.

The Royal Institute of Public Health.—A course of lectures and discussions on "Public Health Problems under War and after War Conditions," will be held in the Lecture Hall of the Royal Institute of Public Health, 37, Russell Square, London, W.C., on Wednesdays in January, February, and March, 1917, at 4 p.m. The course is intended primarily for Fellows and Members of the Royal Institute of Public Health. Medical Officers of Health, Medical Practitioners, Sanitarians, and others engaged in Public Health Work and National Services are cordially invited to attend.

Lectures.

- Jan. 17.—"Principles of Organisation and Administration in Child Welfare Work," by Miss Janet Lane-Clayton, M.D., D.Sc.
- Jan. 24.—"The Prevention and Arrest of Venereal Disease in Women," by Mrs. Mary Scharlieb, M.D., M.S.
- Jan. 31.—"The Prevention and Arrest of Venereal Disease in Men," by Chas. John Macalister, M.D., F.R.C.P.
- Feb. 7.—"The Role of the Midwife and the Protection of Motherhood," by Lady Barrett, M.D., M.S.
- Feb. 14.—"The Prevention and Arrest of Infectious Disease in War Time," by Lt.-Col. S. A. M. Copeman, M.D., F.R.C.P., F.R.S., T.D.
- Feb. 21.—"The Tuberculosis Problem in War Time," by T. D. Lister, M.D., M.R.C.P., F.R.C.S.
- Feb. 28.—"The Protection of the Milk Supply," by Wm. G. Savage, M.D.
- Mar. 7.—"The Selection and Preparation of Foods in War Time," by Prof. F. G. Hopkins, M.B., D.Sc., F.R.S.
- Mar. 14.—"The Protection of the Health of Munition Workers," by Edgar L. Collis, M.B. (Oxon.).
- Mar. 21.—"The Hygiene of Occupation in War Time," by Prof. Sir Thomas Oliver, M.D., D.Sc., F.R.C.P., F.R.S.Ed.
- Mar. 28.—"Personal Habits in Relation to Public Health in Time of War," by Lt.-Col. Sir Alfred Pearce-Gould, K.C.V.O., F.R.C.S.

MEETINGS FOR THE WEEK.

- TUESDAY, 23rd.—Royal Institution, 3. "The Old Brain and the New Brain, and their Meaning," by Prof. C. S. Sherrington.
- WEDNESDAY, 24th.—Royal Society of Arts, 4.30. "Relief Work in Belgium," by W. A. M. Goode.
- THURSDAY, 25th.—Royal Institution, 3. "The Strength and Weakness of Romantic Poetry," by Prof. Sir Walter Raleigh.
- Royal Society. "The Dynamics of Revolving Fluid," by Lord Rayleigh. "Spectroscopic Observations on the Active Modification of Nitrogen," by Hon. R. J. Strutt. "Magnetic Induction and its Reversal in Spherical Iron Shells," by J. W. Nicholson and E. Wilson. "The Two-dimensional Motion of a Plane Lamina in a Resisting Medium," by S. Brodetsky.
- FRIDAY, 26th.—Royal Institution, 5.30. "Epicurean Philosophy," by Prof. G. Murray.
- Physical, 5. "A Clock of Precision," by C. O. Bartrum. "Effect of Water Vapour in the Atmosphere on the Propagation of Electromagnetic Waves," by F. Schwes.
- SATURDAY, 27th.—Royal Institution, 3. "The Lakes and Mountains of Central Africa," by A. R. Hinks.

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CHEMISTRY IN RELATION TO NATIONAL AFFAIRS.*

By Sir WILLIAM A. TILDEN, F.R.S.

THE subject chosen for this occasion is a very large one and for its complete treatment would require many evenings. It will be necessary, therefore, to select a few of the more important from the several lines of thought which suggest themselves.

Partly on this ground, therefore, I have not attempted to enter into the economic features of the questions relating to the industrial applications of chemistry, and how they are to be succoured and sustained under the conditions prevailing after the conclusion of the war. I have also referred only in general terms to the way in which chemistry should be taught and to the conditions under which scientific chemists may assist manufacturing operations.

Though many students of chemistry are present there are many others among the audience who are unacquainted with chemistry, and for their benefit I shall therefore begin by sketching in the briefest possible manner the main features of the history of the science. It is perhaps scarcely realised by many persons, even students of chemistry, how completely it belongs, as a systematic branch of physical science, to modern times. This consideration becomes vivid in my own mind when I reflect that in the early days of my own grandfather, whom I knew personally, as he died long after I was grown up, the composition of air and water was unknown. Oxygen was discovered by Priestley in 1774, the composition of water was determined by Cavendish in 1781, and subsequently the nature of the process of combustion and the influence of air in respiration, in the rusting of iron and other natural processes, were first correctly explained by Lavoisier.

The chief epochs following the time of Lavoisier may be briefly enumerated as follows:—The first twenty years of the nineteenth century witnessed the wonderful discoveries of Sir Humphry Davy and the introduction of the Atomic Theory by John Dalton. This theory has furnished the framework of all chemical theory since that day. Then followed the work of Faraday, to whom chemistry is indebted not only for the discovery of benzol, but especially for the establishment of the laws relating to electrolysis or electro-chemical decomposition. The composition of so-called "organic" compounds such as sugar, alcohol, and acetic acid was not known with certainty much before 1830, and the question as to the composition and constitution of organic substances of all kinds was the chief subject of debate from that time onward for some forty years. With regard to the elements and their simpler compounds, the law of periodicity among atomic weights discovered by John Newlands in 1864, and subsequently established and developed by the great Russian chemist, Mendeleff, has been the guiding principle down to the present day.

With regard to useful applications of chemistry, it may be stated that there were no manufactures based on chemical principles before the discovery of the composition of air and water and the nature of the process of burning.

For ages various chemical arts had been practised. Thus, the mummy cloths and remains of glass vessels to be seen in the British Museum prove that the arts of the

dyer and glass maker were practised long before the Christian Era. Soda and soap were also made by crude processes, and several metals were extracted from their ores, but in no case was the relative chemical change understood.

Let us look at the history of the two chemical substances which supply the keys to nearly all the products of chemical manufacture, namely, sulphuric acid and soda.

Sulphuric acid was originally made by distilling green vitriol, and in the concentrated form still goes by the alchemical designation *oil of vitriol*. But it was observed long ago, that when sulphur is burned a small quantity of the same acid is produced, and an accidental observation led to the discovery that when sulphur is deflagrated with a little nitre, a large quantity of acid is produced. This method was used in the early part of the eighteenth century, and to facilitate the mixture of the fumes on a larger scale, Dr. Roebuck, of Birmingham, introduced the use of a chamber made of sheet lead, and he set up works at Preston Pans in Scotland in the year 1749. The product was known as English oil of vitriol, but no further improvements were possible till the general nature of acids, bases, and salts had been explained by Lavoisier. Then in the nineteenth century the chambers were greatly enlarged, and the first definite improvement in the form of the Gay-Lussac tower was introduced. This method of manufacturing sulphuric acid will probably be superseded in time by the modern contact process.

The history of soda is somewhat similar. Originally obtained wholly from the ash of sea-weeds, and especially of certain plants growing near the sea, soda in the eighteenth century found its way into commerce chiefly in the form of what was known as *barilla* from Spain. But during the war at the end of the eighteenth century Spanish barilla was excluded from France. The French Government accordingly offered a prize for the invention of a process by which soda (the carbonate) could be made from common salt, then largely extracted from sea-water in the neighbourhood of Marseilles. The result was the introduction of the "black-ash" process by Nicholas Leblanc, who set up the first alkali works in 1804.

Leblanc's process was largely adopted in Lancashire and on the Tyne, and during the former half of the nineteenth century sulphuric acid and soda were supplied to almost all the world by England. It may safely be asserted that, without the knowledge of saline compounds and their constitution provided by Lavoisier, the chemical transformation of sodium chloride into sodium carbonate would never have been accomplished, or even attempted.

The supply of dye-stuffs provides another instance of the application of the same principle. Previously to 1856 the dyes required, whether for application to silk, wool, or cotton were obtained almost entirely from vegetable materials such as woods, barks, berries, or extracts. Everyone has heard of madder, logwood, indigo, and the French purples made by macerating certain lichens in ammonia. To these must be added one important dye of animal origin, namely, cochineal. This consists of the bodies of insects which are cultivated in Mexico, the Canary Islands, and other tropical regions. It does not seem long since the British army was clothed in scarlet derived from cochineal. But in 1856 the first of the now extensive series of coal-tar colours, namely aniline purple, or *mauve*, was discovered by the late Sir William Henry Perkin. Many persons now living can remember the magnificent display of crystallised colouring matters, especially the crown shaped frames covered with magenta, which appeared in the International Exhibition of 1862. They can also remember the talk at that time, and for some years later, of the huge dividends being paid by the great firm of English colour-makers, Messrs. Simpson, Maule, and Nicholson.

To realise the predominant position of England in regard to chemical manufactures fifty years ago, it is only necessary to refer to the Reports of the Juries, in

* An Address given at Birkbeck College, on Founders' Day, December, 1916.

connection with the Great International Exhibitions of 1851 and 1862. Not only did the number of exhibits, and the medals and other honours, awarded to the United Kingdom, exceed those of any other country, but the writer of the Report in 1862, no less a person than Prof. Hofmann, then director of the Royal College of Chemistry in London, described the position in the following words:—

"The contributions of the United Kingdom and in particular the splendid chemical display in the Eastern Annex prove the British not only to have maintained their pre-eminence among the chemical manufacturers of the world, but to have outdone their own admitted superiority on the corresponding occasion of 1851."

With such a record from the past and remembering the repeated warnings and appeals which have been addressed by the most eminent British chemists to British manufacturers during the last forty years it was bitterly disappointing to find at the outbreak of war in 1914 that England made only about *one-tenth* of the quantity of dyes required in the Yorkshire dyehouses and that in the preceding year she had paid to Germany a sum of about one and three-quarter millions sterling for these commodities. It was found at the same time that we were practically destitute of many of the synthetic drugs which have become indispensable in recent times, and which, being the products of the chemical laboratory associated with the production of dyes, had been made chiefly in Germany.

The conditions which have led to this state of things have been the subject of much debate, and whether they can be rightly referred to the neglect of organic chemistry in the Universities, or to the patent laws, or to fiscal regulations relating to the industrial use of alcohol, cannot now be discussed. It will be more profitable to look at the present position and see what can be done to recover lost ground.

Happily, very encouraging reports have been given in regard to progress made in the production of dyes in this country, and if it had not been necessary to employ so many of our chemists in making explosives, a business in which few of them had previously any experience, it is probable that the supply would have been by this time not much behind the demand. Some substantial progress has also been made in regard to drugs, and though still dear, there is no serious deficiency.

British chemists have in fact shown themselves fully equal to the demands which have been imposed on them. We require, however, a much larger number of well-qualified men.

Another direction in which chemistry has come to the rescue is in the investigation of the composition of optical and chemical glasses undertaken since the beginning of the war. And as a result several manufacturers have adopted the English formulae, and are providing material independently of all foreign supplies for the making of field-glasses and other optical instruments, as well as for the glass flasks, beakers, tubing, &c., required in the many chemical laboratories.

Many other things we still need. Among them potash salts for agriculture, bromine for the production of bromides used in medicine and for use in making some dyes, also a larger quantity of sugar and paper.

The question arises, What industries should we endeavour to establish to make ourselves less dependent on foreign sources of supply? Obviously we cannot make everything, but as we have coal-tar of which the supply can be increased by improving the methods of making coke, we can certainly make dyes and drugs. Sugar we can increase by cultivating the sugar beet in England, but paper must be obtained from countries where timber is grown. A large quantity of paper pulp has been obtained from the northern countries of Europe, but there is Canada with extensive forests which may hereafter give us all we need. There is, therefore, no reason for despair as to the future of chemical industry in the

British Empire provided favourable conditions are established.

First of all, we must have many more well-trained chemists. By this I do not mean dispensers of medicine, or keepers of shops the windows of which are adorned with the familiar bottles of bright colours. I refer, of course, to chemists who have followed faithfully a course of study in the theory and practice of scientific chemistry in one of the universities or technical institutes. Here is an opportunity for women, for there is nothing in the nature of the study itself or in its applications which should be an obstacle to the successful practice of chemistry, analytical, purely scientific, or industrial, by women. But it must be understood by men and women alike that only well-educated people, with a moderate knowledge of mathematics, can hope with diligence to reach the higher grades of the profession.

In the next place co-operation among manufacturers is very desirable. Already some important steps have been taken in this direction, and when, a few months ago, it was announced that an alliance had been established between Brunner, Mond, and Co., and the Castner-Kellner Company, it was felt that one of the most satisfactory possible movements toward strengthening British chemical industry had been accomplished. Since that time a powerful Association of Chemical Manufacturers has been formed, which includes many other important firms. In place of rivalry and unrestrained competition at home we may look forward to a condition of mutual help, remembering always that the fiercest competition of all comes from over the sea.

In the third place, henceforth, a better position for the chemist in public esteem, social position, and official recognition, will be demanded. The ignorance of all science among the British public is at present scandalous, and this is largely attributable to the neglect of science in the schools, which are still dominated by people brought up in exclusively classical traditions. Nor will it be tolerable that a Government Department should again place chemists in the same category as navvies and labourers, as was the case not many months ago. The education and training of a professional chemist extends over several years, and the cost both in time and money is approximately equal to the cost of gaining entrance to the profession of medicine. If conditions as to pay and prospects are not substantially improved the majority of able young men in this country will continue to be attracted into the ranks of the law, medicine, engineering, and commerce, and the supply of properly qualified chemists will remain as insufficient as at present.

The recent announcement of a new Committee of the Privy Council with power to give large pecuniary assistance to research, is encouraging, but not entirely satisfactory, because it is apparently going to be administered from Whitehall, where there is no science, and scientific men have no place. In the great councils of the nation, in public offices, in business, and in education, science at present occupies only a subordinate position. There has been usually only one man of recognised scientific position in the House of Commons, and as far as my memory serves me, there have only been two scientific men admitted into the Privy Council. These were Professor Huxley and the late Sir Henry Roscoe, and on the decease of the latter in 1915, no step has been apparently taken to fill his place. This is not as it should be, and when the war is over it will be found that scientific men will no longer be content with smooth words from ministers without that practical acknowledgment of the indispensable value of their services which is their due.

As to manufacturers, they have long held back from the utilisation of scientific assistance, and in many cases have met with such a measure of commercial success as seemed to justify this attitude. The time has, however, gone by when traditional processes in the works, traditional methods of business, or even acknowledged excellence in quality of goods will suffice to sustain this position of

prosperity. It has become apparent to the more progressive of the great firms that permanent prosperity can only be secured by making use of every new discovery which in any way affects their processes, and they have accordingly engaged the services of competent scientific men at reasonable rates of remuneration. Those who have not taken this course will certainly be overtaken by the fierce competition which is certain to arise in these rapidly changing times, and it may safely be asserted that permanent industrial success can only be secured by following the road in which science is chosen as the guide.

THE TRAINING OF THE ANALYST.

By FRANK BROWNE, F.I.C.,
formerly Government Analyst, Hongkong.

THE education of the scientific man, to be of practical utility, should have the broadest foundation. Excellent as the instruction may have been, the period of tuition is with many, probably with most students, too much curtailed. A chemical student on leaving college may have obtained a very good degree, and yet may know little of the practical side of the analytical profession. Is it not true that to many such even the recognition of a simple salt of a common metal is by no means easy, and is arrived at frequently only after an undue expenditure of time? And is there possessed that thorough knowledge of the British system of weights and measures so that ordinary problems can be worked out without a long circuitous process of calculation? Or give a sample of boiler incrustation and ask for the constituents present, and roughly the proportion of each. Is it not a fact that, although a correct answer may be given in, the amount of time expended has been altogether disproportionate to what should be taken over such an examination? It is not here asserted that all newly qualified men are lacking to the extent indicated, but there seems to be with many a deficiency of analytical experience, which is likely to hamper them in after life. This article is not written for any controversial purpose, but is rather the reflections of one who, after long absence from England, is able to take a detached view of what seems to be some defects in our educational system as applied to the analyst. A graduate who has adopted a chemical career may go direct from his college to a public analyst's laboratory, and there it may be that he will not suffer much from having had academic training only. He would be given work to suit his capacity, and as he obtained more experience the analyses given him to perform would become more difficult. There, with a large variety of examinations, the processes used will be of a standard and rapid kind, and after a year or two the assistant of ordinary ability becomes highly useful. Take the case of this same student supposing he has entered a works laboratory. Here, also, by constantly going over routine processes, he may become very helpful to his employers. But here there may be plant difficulties to be solved, and now, although well trained and capable of carrying out analyses satisfactorily as long as he is given unlimited time, he may be found wanting on account of his lack of knowledge of good rapid analytical methods. Here, for the most part, difficulties have to be solved with as little interference as possible with laboratory routine, and it is reasonable to suppose that an employer feels disappointed when an assistant, well recommended from his college, seems unable to carry out in a commonsense practical manner a very ordinary analysis. Perhaps it is desirable to go outside routine work and ascertain accurately the composition of some new material used on the works, such as an oil, alloy, or cement. Now, in a laboratory where such substances are examined frequently, the analysis would be concluded after at the most three or four hours. In a laboratory where such an examination is outside the usual scope, much longer

might be necessary, but at any rate the training of an analyst ought to be such that he can work out a process from a work of reference, and apply it successfully to the substance in question without interfering greatly with his routine duties.

It may be of interest to young analysts to know that almost any system of analytical examination may be so carefully studied with a view to speed as to be almost incredibly shortened. A cement analyst informed me that, working single-handed, he was able to determine quantitatively in one hour the silica, iron, alumina, lime, magnesia, and loss on ignition of ordinary cement. Another wrote me that he was now able to determine the amounts of antimony, iron, lead, and arsenic in *antimony ochre* in two hours, and the same in two *stibnite* ores in three hours. Perhaps a few remarks as to speed in performing analyses may be found useful. It may frequently be obtained by bearing in mind that it is most helpful in performing a new analysis to write down in what direction the process may perhaps be shortened by the introduction of, say, a volumetric for a gravimetric process, which is nearly always possible in inorganic work. And when a good process of estimation has been arrived at it may be better understood by ascertaining the effect of varying conditions—such as the concentration of the solution to be examined, the strength of the volumetric reagent to be added, and the rapidity with which the latter may be run in, and so on. In this way sources of error may be discovered and guarded against and invaluable experience obtained. On no account should it be considered that no improvement is possible in a process, even although such is taken from a good textbook. Many excellent methods of examination are locked up in laboratory journals, and are not likely to be published except, perhaps, after the lapse of some years. When physical constants, such as the relative density and refractive index, are to be determined frequently, a table of corrections for temperature is simply invaluable.

Sometimes in routine examinations the use of a pipette to deliver a constant weight (CHEMICAL NEWS, July 28, 1916, p. 41) may prove a great time-saver. Also standard solutions can be made often so that 1 cc. corresponds to 1 per cent when 1 gm. of substance is taken. This is a good system, and saving of time and error. With every analyst the time comes when, from some cause or other, there is an apparent deficiency of work in the laboratory. This period in reality is most valuable for maintaining efficiency. Everyone during his busy days will see matters, such as the testing of new processes, that cannot at once be attended to, and these inquiries should be entered at the end of his note-book for further consideration when opportunity permits.

Now, the student in his academic course of practical work has no time to do more than carry out typical analyses, so that the writer desires particularly to support the useful and practical recommendation of Mr. A. Chaston Chapman, formerly President of the Society of Public Analysts and Other Analytical Chemists, as set out in his Annual Address (CHEMICAL NEWS, 1916, cxvii., 69) that:—

"So far as our colleges are concerned I feel very strongly that a more thorough training in analytical chemistry is desirable, and I would in addition venture to suggest that the present curriculum of those chemical students who intend to become professional chemists should whenever possible be amplified so as to include a further year of study.

"During this post-graduate year the student should be trained by thoroughly competent and specially selected teachers under conditions approximating more to those of the technical than to those of the academic laboratory."

It is a matter of opinion as to what would be the course of study during this year that would develop best the powers of the student. The programme might include:—

Water analysis for industrial purposes. Fuel (coal), determinations of volatile combustible matter, water, ash, sulphur (by several methods), and calorific value by cal-

culatation and by experiment. Oils, fats, and waxes—determination of constants and examination of several adulterated specimens. Alcohol—estimation in beer, wine, and spirits, by several methods, and determinations of very small quantities in liquids. Metals and alloys—quick methods for ascertaining the amount of the principal metal in commercial tin, lead, antimony, copper, zinc, and in molybdenite. Also working over a few alloys of these metals in order to determine the proportion of each constituent metal. A good working acquaintance with the microscope, polarimeter, various forms of refractometer, and spectroscope.

In this course some time should be given to the recognition of substances, organic and inorganic, and if the student does not feel able to determine with precision after a few minutes the nature of any ordinary simple inorganic substance not requiring fusion with other substances to bring into a soluble form, he should practice until he finds out where he is deficient. As regards so-called insoluble substances, these characteristic should be studied individually together with the best means of recognition. Commonly occurring organic substances should be examined so that a fair number may be recognised. Out of the way compounds may occasionally be met with, but for these considerable help ought now to be obtained from the text-books which should have formed, or are forming, part of the student's ordinary reading course. Students would now have an opportunity of getting more proficient with the slide rule in their calculations. And a good sound knowledge of the British system of weights and measures might be acquired by expressing some results in grains per gallon, per pound, or per cubic foot. In order to promote business habits the students should be expected to be industrious and to observe closely laboratory hours. After the completion of each kind of analysis they should, from their laboratory note-books, either card-index the process used, or adopt some other means of permanently recording their work in good detail.

Students who have been through a course such as that suggested would read current literature with much more interest, and would ever be seeking out new methods and labour and time-saving devices. Moreover, they could not fail to obtain a sound knowledge also of theoretical and physical chemistry—a knowledge which, in their careers, will allow no technical process coming under their cognisance to pass without understanding thoroughly, as far as it is possible, the chemical or physical effect produced by each and every substance employed. Such a course could not fail to improve the capacity of a student for research. It would give him a good sound grip of analytical chemistry, and would tend to render the student's knowledge much more assimilable, and the student himself much more valuable to his future employers.

ON THE RATES OF SOLUTION OF METALS IN FERRIC SALTS AND IN CHROMIC ACID.*

By R. G. VAN NAME and D. U. HILL.

(Continued from p. 29).

Rates of Solution in Chromic Acid.

In the experiments with chromic acid as oxidising agent the solutions were initially about 0.015 molar with respect to CrO_3 , and contained also definite known amounts of free sulphuric acid. The precaution, employed with ferric salts, of keeping an atmosphere of carbon dioxide above the liquid during the reaction, was, of course, unnecessary in working with chromic acid, but in other respects the procedure remained as before. As compared with the case of ferric salts, a higher concentration of hydrogen ion is essential for the reaction to proceed smoothly, and a

further difference exists in the fact that the acidity decreases during the reaction. But unless the initial acidity is low this decrease is relatively small. In the experiments accepted as trustworthy, the initial acidity was always 0.5 normal (0.25 molar H_2SO_4) or above, and the decrease in acidity, even in the extreme cases, was only about 6 per cent—an amount too small to have any marked effect upon the observed reaction velocity.

The analyses of the solution samples for chromic acid were carried out by one or the other of the two following methods:—(a) Treatment with an excess of potassium iodide and titration of the liberated iodine with thio-sulphate; (b) treatment with a known volume of standard ferrous sulphate and titration of the unoxidised ferrous sulphate with permanganate.

Method a, which was conducted according to the directions of Seubert and Henke (*Zeit. Angew. Chem.*, 1900, 1147), was applicable only in certain cases, and seemed to have no advantage in accuracy over Method b. The experiments in which Method a was used are designated in the tables by asterisks. Full experimental data are given for Experiment 1, the values of c being volumes of 0.02 normal thio-sulphate used, which are evidently proportional to the concentrations of chromic acid at the corresponding times, and can therefore be directly substituted in the velocity equation in calculating k .

Method b was applicable in all cases, and was on the whole preferred, after experience had proved that the presence of the green chromic salt in the solution did not seriously diminish the sharpness of the permanganate end-point. Data for a typical experiment (No. 4 of Table IX.) are given in detail, the values of c being here cubic centimetres of 0.02 normal permanganate used in titrating 20 cc. of the given ferrous sulphate solution after the addition of the 20 cc. sample of solution to be analysed, together with a little phosphoric acid. The concentration of chromic acid is measured, in terms of the ferrous sulphate solution, by the expression $20-xc$, in which x is the volume of the ferrous sulphate equivalent to 1 cc. of the permanganate. This expression was used in calculating the velocity constants.

Cadmium and Copper.—Table IX. gives the results obtained with cadmium and with copper in solutions 0.25, 1.25, and 5 molar with respect to sulphuric acid. Both metals under these conditions behaved normally, giving satisfactorily constant reaction velocities, and the values obtained for the two metals are, moreover, in excellent agreement with one another throughout.

On the other hand, a few experiments conducted in solutions only 0.05 molar with respect to sulphuric acid gave distinctly abnormal results, the reaction velocities showing progressive variation, and no approach to agreement between cadmium and copper. Since these experiments were plainly affected by specific disturbances arising from insufficient acidity, the results, though included in the table, are of little significance.

Iron.—The experiments on the rate of solution of iron in chromic acid are complicated by the fact that the oxidation takes place in two stages. Two examples of such two-stage reactions have already been considered, tin in ferric sulphate and copper in ferric chloride, but in both cases the method of analysis was such that the second stage of the oxidation had no direct effect upon the titre of the solution. Consequently, the concentration of the oxidising agent, as calculated from the titrations and used in calculating the velocity constant, was in reality the combined concentrations of two oxidising agents present in unknown proportions in the solution, namely, the ferric salt, and the higher oxidation product of the dissolving metal. In the present case it is the concentration of the chromic acid alone which is given by the titrations, and therefore both stages of the oxidation change the titre of the solution. This difference must be borne in mind in comparing the results.

Now, in general, in a two-stage reaction of this type between a metal and a dissolved oxidiser, if the second

* From the *American Journal of Science* xlii., 301.

TABLE IX.—Cadmium and Copper. ClO_3 , 0.015 molar.

No. of expt.		Cadmium.								K.
		H_2SO_4 , 0.25 molar.								
*1.	$v =$	580	560	540	520	500	480	460		
	$\Delta t =$	10	10	10	10	10	10	10		
	$c =$	48.11	42.68	37.74	33.14	28.96	25.13	21.72	18.60	
	$k_1 =$	6.94	6.88	7.02	7.00	7.08	6.99	7.13		
	$k =$	6.96	6.88	7.02	7.00	7.08	6.99	7.13	7.01	
*2.	$k =$	7.04	7.13	7.00	7.08	6.99	7.00	7.05	7.04	
		H_2SO_4 , 1.25 molar.								
3.	$k =$	5.16	5.41	5.31	5.29	5.47	5.23	5.37	5.32	
		H_2SO_4 , 5 molar.								
(a) 4.	$v =$	580	560	540	520	500	480	460		
	$\Delta t =$	10	10	10	11	9	10	10		
	$c =$	6.25	8.32	10.28	12.30	14.50	16.22	18.14	20.03	
	$k_1 =$	2.71	2.60	2.71	2.73	2.63	2.68	2.68		
	$k =$	2.71	2.59	2.71	2.73	2.63	2.69	2.68	2.68	
5.	$k =$	2.64	2.61	2.70	2.57	2.72	2.70	2.58	2.65	
		H_2SO_4 , 0.05 molar.								
*6.	$k =$	8.59	8.54	8.33	7.94	8.23	7.54	7.81	8.14	
*7.	$k =$	8.48	8.65	8.16	7.82	7.82	7.89	7.39	8.03	
		Copper.								
		H_2SO_4 , 0.25 molar.								
8.	$k =$	7.18	6.79	7.06	7.05	6.73	7.21	6.95	7.00	
9.	$k =$	6.75	6.96	6.91	7.07	6.88	6.84	6.87	6.90	
10.	$k =$	6.96	6.86	6.95	6.99	7.00	7.09	6.85	6.96	
		H_2SO_4 , 1.25 molar.								
11.	$k =$	5.47	5.29	5.39	5.31	5.34	5.23	5.36	5.34	
		H_2SO_4 , 5 molar.								
12.	$k =$	2.73	2.67	2.72	2.73	2.78	2.72	2.76	2.73	
13.	$k =$	2.71	2.64	2.76	2.75	2.76	2.69	2.67	2.71	
		H_2SO_4 , 0.05 molar.								
14.	$k =$	2.44	4.02	5.50	6.20	6.76	7.02	7.11	5.58	
* Chromic acid determined by iodometric method.										
(a) 1 cc. $\text{KMnO}_4 = 0.383$ cc. FeSO_4 .										

* Chromic acid determined by iodometric method.

(a) 1 cc. $\text{KMnO}_4 = 0.383$ cc. FeSO_4 .

stage is sufficiently rapid the lower oxidation product will be oxidised where it is formed; that is, at the surface of the metal. Thus it may happen that a metal in passing through two stages of oxidation gives the same velocity constant as a metal undergoing only one stage, the observed velocity being that of the diffusion process. Such an instance is apparently offered by the case of tin in chromic acid, to be discussed later. On the other hand, if the second stage of the oxidation is not quite rapid enough to produce the result just mentioned, some of the molecules of the lower oxidation stage will not be oxidised until they have diffused part way through the diffusion layer, or, perhaps, have passed through it into the solution. The effect in either case is to shorten the average length of the diffusion path for the molecules of the oxidising agent, and therefore to raise the observed reaction velocity. The reaction between tin and iodine dissolved in potassium iodide solution probably belongs to this category, as has been shown elsewhere (*Am. Journ. Sci.*, 1911, [4], xxxii., 216). There is, moreover, reason to expect similar behaviour from iron in chromic acid, for Benson has shown that the reaction between chromic acid and ferrous sulphate progresses in dilute solutions at a rate sufficiently slow to be easily measurable (*Journ. Phys. Chem.*, 1903, vii., 1).

The results obtained, shown in Table X., Experiments 1—5, are in accordance with this view. Not only are the constants higher throughout than with the other metals under like conditions, but they also show the continuous rise which would be predicted from the accumulation of

ferric salt, which itself reacts with the metal, producing ferrous salt in constantly increasing proportion compared with the chromic acid, and thus causing a progressive shortening in the average length of the diffusion path.

In Experiments 1—4 the titrations were carried out during the progress of the experiment, and with very little delay. Now, Benson has shown, in the article just cited, that ferric salts have a retarding effect upon the oxidation of ferrous salts by chromic acid. If in our analyses the time allowed for the completion of this reaction had been too short this would have produced high and rising velocity constants. That the high and rising constants actually observed were not due to this is proved by Experiment 5, in which the solution samples, after mixing as usual with a known amount of ferrous sulphate, were allowed to stand for two and a half hours before titrating back with permanganate. It is evident that this modification made no appreciable difference in the results.

Nickel.—The experiments with nickel in chromic acid were carried out in solutions either 0.25 or 5 molar with respect to sulphuric acid. In the former solution the velocity constants were in all cases irregular and abnormally low; in the latter the results were apparently normal, and agreed well with the values obtained with cadmium and with copper under like conditions.

The nickel discs after use always showed traces of a blackish deposit, or, in the stronger acid, of a brownish discoloration, these surface coatings resembling closely in appearance and amount those observed with nickel in ferric sulphate solutions of like sulphuric acid concentra-

TABLE X.— CrO_3 , 0.015 molar.

No. of expt.		Iron.								K.
		H_2SO_4 , 0.25 molar.								
(a) 1.	$v =$	580	560	540	520	500	480	460		
	$\Delta t =$	10	10	10	10	10	10	10		
	$c =$	6.95	13.87	20.02	25.60	30.60	35.10	39.17	42.70	
	$k_1 =$	9.67	9.85	10.36	10.93	11.82	13.25	14.86		
	$k =$	9.66	9.85	10.37	10.94	11.83	13.25	14.86		11.54
2.	$k =$	9.61	10.39	10.34	11.02	12.10	14.09	15.22		11.82
		H_2SO_4 , 5 molar.								
3.	$k =$	3.78	4.16	4.14	4.14	4.08	4.27	4.49		4.15
4.	$k =$	3.96	4.10	4.12	4.19	4.39	4.52	4.49		4.25
5.	$k =$	3.93	3.99	4.11	4.32	4.31	4.24	4.48		4.20
		Nickel.								
		H_2SO_4 , 0.25 molar.								
(b) 6.*	$k =$	5.75	5.95	5.80	5.40	5.80	5.54	6.12		5.77
(a) 7.*	$k =$	4.71	6.00	6.92	6.76	7.05	6.80	6.80		6.43
(a) 8.*	$k =$	5.92	4.56	3.48	2.71	3.27	3.40	3.51		3.84
(c) 9.*	$k =$	0.49	1.54	1.35	0.03	1.71	0.09	1.04		0.89
(d) 10.*	$k =$	0.37	5.96	6.01	5.67	4.48	3.68	4.82		4.43
		H_2SO_4 , 5 molar.								
11.	$k =$	2.55	2.64	2.70	2.66	2.58	2.78	2.56		2.64
12.	$k =$	2.61	2.71	2.72	2.71	2.69	2.75	2.71		2.70
		Tin.								
		H_2SO_4 , 5 molar.								
13.	$k =$	2.76	2.72	2.80	2.72	2.68	2.68	2.78		2.73
14.	$k =$	2.84	2.74	2.78	2.72	2.66	2.73	2.74		2.74
		Silver.								
		H_2SO_4 , 0.25 molar.								
15.	$k =$	4.51	4.30	4.28	4.24	4.52	4.54	4.40		4.40
16.	$k =$	4.31	4.43	4.02	4.25	4.03	4.22	4.15		4.20
17.	$k =$	4.35	4.17	4.35	4.10	4.21	4.24	4.17		4.23
		H_2SO_4 , 5 molar.								
18.	$k =$	(1.53) (e)	1.26	1.20	1.18	1.21	1.23	1.24		1.22
19.	$k =$	(1.52) (e)	1.28	1.29	1.21	1.21	1.18	1.19		1.23

Initial Velocities by Extrapolation.—Expt. 15, 4.40; Expt. 16, 4.27; Expt. 17, 4.28; Expt. 18, 1.22; Expt. 19, 1.31.

* Chromic acid determined by iodometric method.

(a) 1 cc. $\text{KMnO}_4 = 0.385$ cc. FeSO_4 .

(b) Disc immersed in dilute HCl in contact with zinc.

(c) Disc cleaned with 2 : 1 HNO_3 after each reaction period.

(d) Disc cleaned with warm 1 : 2 HNO_3 after each reaction period.

(e) Not included in average.

tion (see p. 10 ante). The effect of these coatings upon the reaction velocity was apparently negligible in 5 molar sulphuric acid, and even in the weaker acid they were probably responsible for only a small part of the abnormality observed.

The chief cause of the low and variable results obtained in the presence of 0.25 molar sulphuric acid was the tendency of the nickel disks to become passive. In Experiments 6, 7, and 8, to insure activity of the disc at the start, after cleaning in the usual manner it was immersed in dilute hydrochloric acid and thoroughly rubbed under the acid with a zinc rod. This treatment did not make the constants regular. Since low constants are found following much higher ones (notably in Experiment 8) passivity must have been produced in the chromic acid solution. That the reaction velocity also increases at times during the course of the experiment is perhaps explained by the fact that a partly passive disc in sulphuric acid would constitute a short-circuited element of which the active areas would be the anodes, and the adjacent passive areas would consequently be subject to cathodic reducing effects

which would tend to destroy their passivity in so far as it was not re-established by the chromic acid. No explanation is offered for the fact that these two opposing tendencies produce fluctuations in the degree of passivity. It may only be suggested that the variations are in some way connected with the gradual uncovering of impurities in the metal.

In Experiments 9 and 10 the attempt was made to restrict so far as possible the formation, on the disc, of the blackish deposits above mentioned, by removing the disc from the solution at the end of each reaction period and cleaning with nitric acid. The treatment with a zinc rod was omitted. Neither hot concentrated hydrochloric acid nor iodine in potassium iodide solution would remove the deposit completely. Concentrated nitric acid removed it easily and gave the metal a perfectly clean surface, but a disk so cleaned was invariably wholly passive and was no longer attacked by the chromic acid solution. Nitric acid of two thirds strength was accordingly selected for trial in Experiment 9, but proved too strong, the results showing practically complete passivity during two of the

reaction periods and a very low activity during the rest. The more dilute nitric acid used in Experiment 10 produced high passivity during the first reaction period, but the later constants showed no more passivity than might be expected, according to the results of Experiments 6, 7, and 8, from the action of the chromic acid alone.

For Experiments 11 and 12 the sulphuric acid concentration was increased to 5 molar with very beneficial results. The absence of any indication of passivity in these experiments seems to prove that this concentration of sulphuric acid was sufficient to entirely overcome the tendency of chromic acid to produce passivity in the nickel discs. The rate of the reaction shows a satisfactory constancy, and the mean value of the velocity constant agrees with the values obtained with several other metals under like conditions.

Tin.—The study of tin in chromic acid solution was confined to the two experiments numbered 13 and 14 in the table, both conducted in the presence of 5 molar sulphuric acid. The results are in both cases apparently normal, and the reaction velocity has the expected value. This behaviour on the part of a metal-forming soluble and stable salts of two different valencies indicates one of two possibilities; either (a) the second stage of the oxidation does not occur to a measurable extent (the case observed with tin in ferric sulphate), or, (b) the second stage is so rapid that no appreciable diffusion of stannous salt away from the metal can occur. As the reaction between stannous sulphate and chromic acid is practically instantaneous there can be little doubt that explanation (b) is the correct one here.

Silver.—Experiments with silver in chromic acid gave the values recorded in Nos. 15—19 of Table X. In general, the results resemble those given by silver in ferric sulphate, both in the relatively low reaction velocities observed and in the fact that the velocity tends to decrease as the silver salt accumulates in the solution. On account of this decrease the reaction velocity characteristic of a given experiment is best represented, as in a number of cases already considered, by the "initial velocity," found by extrapolating back to time zero.

To be continued,

REPORT OF THE CHEMIST, DEPARTMENT OF AGRICULTURE, BUREAU OF CHEMISTRY, WASHINGTON, D.C., U.S.A.

(Concluded from p. 33).

Enforcement of Food and Drugs Act.

Domestic Foods and Drugs.—Five hundred and seventy-seven recommendations for seizure and 787 recommendations for criminal prosecution were made through the office of the Solicitor to the Department of Justice. The work with the Bureau of Standards to establish "tolerances and reasonable variations" under the net-weight amendment has progressed, that upon dairy products being completed. Among the 1036 cases of all kinds terminated in the courts during the year were 198 alleging false and fraudulent labelling of medicines, in all of which save five the courts found for the Government. In one food case a sentence of imprisonment was imposed. A number of indictments for conspiracy were found, upon evidence obtained by the bureau, concerning the adulteration of olive oil, domestic traffic in refuse eggs, traffic in refuse eggs exported to England, and the sale of spurious synthetic drugs.

There were collected 4483 official samples. These showed an increasing percentage of substantial violations, an index not of increased disregard of the law, but, as pointed out in the report last year, solely of greater discrimination in the selection of samples. In addition an increased number of informal samples, about 4000, were

taken, because these demand less labour and yet are adequate for the routine checking of staple products to gauge the effect of the bureau's action, and for general surveys preliminary to definite campaigns. The number of official samples analysed by the field force is given in Table I. The use of the guaranty legend and serial number ceased very largely during the year.

In the Service and Regulatory Announcements were published 52 opinions and 600 notices of judgment.

All the work on the certification of colours was concentrated in Washington. The laboratory at New York City was transferred to new and more commodious quarters in the United States Appraiser's Stores. The St. Paul laboratory was moved into the new Federal building in Minneapolis. The dairy laboratory was abolished and its work distributed among other laboratories of the bureau.

A separate office has been established to deal with cases of false and fraudulent labelling of medicines and mineral waters under the Sherley amendment to the food and drugs act. To this office are also referred such medical matters as may arise in connection with the work of the bureau. At the request of the Secretary an officer of the United States Public Health Service was detailed to take charge. In consequence this work has been carried on more expeditiously and efficiently than heretofore.

A very close inspection was maintained during the past year over the early shipments of oranges and grapefruit. In this campaign the bureau received the active help of the greater part of the citrus fruits producers. Comparatively few sweated, immature oranges or grapefruit were marketed. The better quality of the fruit is believed to have resulted in a steadier market, so that the producer as well as the consumer benefited.

The unusual demand for cotton lint by the munitions factories greatly increased the delinting of cotton seed. The cake and meal made from such delinted seed has usually less protein than that from undelinted seed. Many mills in labelling their product used the analyses of former years, thus misleading the consumer, who, as a rule, was unable to protect himself because of the rising market. With the assistance of State officials, the Bureau has taken action in many cases.

Based upon co-operative sanitary surveys of the waters over oyster beds in certain sections, described in the report for the last two years, the department, by appropriate notice, warned the producers against the shipment interstate of oysters from such sections during the fall, spring, and summer, when the oysters are not hibernating. In the case of particular regions warning of this nature had been issued some few seasons prior to last year. This warning had not been heeded in all cases. Last fall prosecutions were brought, with the result that all shipments from such condemned territory thereafter were stopped in the fall and spring.

Other forms of adulteration not already mentioned that received special attention are: The substitution of mountain maple, *Acer spicatum*, for cramp bark, *Viburnum opulus*, the adulteration of oysters, scallops, and canned tomatoes with water, the substitution of coloured starch paste for tomato sauce, the reprocessing of spoiled canned goods, the traffic in cull beans, in decomposed tomato products, in rancid olive oil, in wormy horse beans, the substitution of foreign fat for cacao butter in, and the addition of cacao shells to, cacao products, the adulteration of rice bran with rice hulls, the colouring of inferior macaroni and of plain noodles, the misbranding of domestic macaroni in simulation of imported goods, and the adulteration of oats with water or weed seeds.

Co-operation with State Officials.—It is not possible to give a complete account of the assistance given State and municipal officials by the Bureau, or of the assistance received by the Bureau from them, because much of this co-operation is of an informal nature and because local officials do not always report to the Bureau upon the value of the information received. However, such co-operation

TABLE I.—Report of Branch Laboratories for year ended June 30, 1916.

Laboratory.	Import samples, analyses.			Floor inspection samples.	Interstate samples, analyses.			Miscellaneous samples.	Total samples analysed.	Hearings held.	
	Legal.	Illegal.	Released without prejudice.		Legal.	Illegal.	Check analysis.			Personal.	By correspondence.
Central district—											
Chicago ..	154	277	47	2612	421	574	174	246	1893	232	133
Cincinnati ..	192	51	4	243	163	176	39	1977	2602	134	326
Minneapolis ..	30	19	5	122	201	187	0	1190	1632	56	62
New Orleans ..	35	112	30	1213	82	127	10	208	604	146	65
St. Louis ..	5	12	1	240	1737	740	23	1744	4262	375	140
Total ..	416	471	87	4430	2604	1804	216	5365	10993	943	726
Eastern district—											
Boston ..	364	453	84	10089	125	343	23	195	1587	439	193
Buffalo ..	9	60	13	43	31	143	0	306	562	64	113
New York ..	4146	2991	1161	31786	102	333	2	161	8899	1224	2221
Philadelphia ..	277	227	101	2973	47	59	2	42	755	360	40
Porto Rico ..	189	596	108	3261	9	94	0	1	997	491	121
Savannah ..	36	39	1	0	84	150	0	25	335	13	39
Washington ..	68	11	1	14	314	304	9	657	1364	13	4
Total ..	5089	4380	1469	48169	712	1426	36	1387	14499	2604	2731
Western district—											
Denver ..	17	6	18	59	60	68	9	102	280	4	25
Honolulu ..	93	207	8	2807	1	2	0	42	353	217	0
San Francisco ..	703	938	113	14398	176	162	23	865	2980	918	251
Seattle ..	131	351	68	6605	76	73	0	340	1042	267	29
Total.. ..	947	1502	207	23869	313	305	32	1319	4655	1406	305
Grand Total	6452	6353	1763	76468	3629	3535	314	8101	30147	4953	3762

has been more effective than ever before owing to the manner in which the Office of State Co-operative Food and Drug Control, established in 1914, has conducted its work, described in a general way in the report of last year, and because of the greater amount of information it has distributed. Many conferences have been held with State officials, and they have been notified of the beginning and termination of court cases, of court decisions, of all public hearings held by the Bureau. Twenty-three sets of information cards on methods of food and drug analysis have been issued to them and they have been furnished copies of analyses and inspection reports. A Manual of Procedure for the Guidance of State Health, Food, and Drug Officials has been compiled and forwarded to State officials for their information and guidance when endeavouring to use the Federal food and drugs acts outlined in Section 5 of the act. A list of Federal and State Dairy, Food, Drug, and Feeding Stuffs Officials has been prepared and kept up to date for the information of these officials. A compilation of State food and drug laws and of State food inspection decisions has been begun. Twenty-three instances of seizure action instituted by State officials are known to the Bureau. Other seizure actions under the Federal law, not reported to the Bureau, were undoubtedly inaugurated by joint action of the State official and the local United States attorneys. One hundred and ninety-one official samples were collected by State officials in 19 States. Among the adulterated articles proceeded against under State laws or municipal ordinances upon information furnished by the Bureau may be mentioned decomposed eggs, decomposed canned goods, decomposed fish and poultry, polluted or watered oysters, watered scallops, saponin-containing foods, liquors containing wood alcohol, misbranded nostrums, and spurious drugs. In a large number of instances information was given to the Health Department of New York City which led to condemnation of adulterated food not coming under the jurisdiction of the Federal act. Many of the State and municipal officials have reciprocated for information of this kind by furnishing to the

Bureau evidence of violations of the Federal law. Among the most notable instances are polluted or watered oysters, watered scallops, adulterated milk or cream, decayed eggs, decomposed canned goods, butter, and fish, wood alcohol in liquors, cottonseed meals and other feeds below guarantee, adulterated oats, and misbranded nostrums. Some specific instances of effective co-operation with State and municipal officials have been mentioned above in connection with other phases of the Bureau's work. Two other types follow:—

Abnormal trade conditions fostered the production of spurious drugs in place of synthetic ones which are ordinarily imported, notably acetyl-salicylic acid and neosalvarsan. Though a number of shipments were seized, a number of individuals successfully prosecuted under the food and drugs act, and indictments returned under the postal laws, the traffic could not wholly be suppressed by Federal action nor the goods in the hands of local dealers in many sections of the country destroyed. The situation was laid before State and municipal officials, who instituted many prosecutions and seizures with the result that through this joint action this fraudulent traffic was broken up.

In co-operation with the food and drug commissioner of Texas, the cause of contamination of certain wells in Texas, the water of which is widely distributed, was determined. When the results were laid before the local authorities steps were taken to remedy the situation. Similar action has been taken in the case of other spas.

The co-operation in the sanitary control of the milk supply of small cities described in the report for last year has been extended in Illinois, Iowa, Missouri, Kansas, Nebraska, and in New England. It is proposed to repeat this work year after year, extending it each year to new territory. In some localities bad conditions were found, due in the main to insufficient cooling and careless handling. Perhaps the best result of this work has been that it stimulated some of the local authorities to take up similar work independently so that definite permanent improvement of the milk supply of a number of cities has

resulted. The co-operative work on the control of the shipment of decomposed eggs described in the report of last year has been extended to cover much of the territory in which shipments originate, so that eggs are now candled before shipment far more than formerly and the spoiled eggs destroyed or fed to poultry and stock. At the same time information given to local officials has helped them to curb local traffic in eggs rejected in candling.

The joint committee on definitions and standards has considered a large number of products. Based upon its recommendations the following food inspection decisions have been issued: No. 160, Gluten Products and "Diabetic" Food; No. 161, Maple Products; No. 162, Egg Noodles and Plain Noodles; No. 163, Cacao Products.

Importations.—The analyses and inspections made in the control of the importation of foods and drugs have been tabulated in Table I. Owing to the unusual trade conditions, while the quantity of imports has been reduced, the variety has not; and there has been such a variation in a single class of products that it has been found necessary to make a great many more examinations of a single importation than were formerly required. This situation is particularly reflected in the quality of the crude drugs and spices received. Prices have been unusually high and the temptation to offer spurious or adulterated articles correspondingly great. The quality of senna leaves, cinchona products, ipecac, and strophanthus was often poor and sometimes a completely spurious article has been offered. The inability to procure certain spices from the usual sources has resulted in the introduction from new sources of new types, some of which were adulterated or spurious. Especial difficulty was encountered with coriander, fennel, celery, anise, cummin, and Chinese and Indian mustard. The poisonous leaves of *Coriaria myrtifolia* were found in marjoram leaves, *Origanum marjorana*. Owing to the increase of the Bureau force of microscopists the control of crude drugs and spices is becoming more effective. Worthy of special mention is the continuation of the exclusion from New England of spoiled Canadian milk and cream. Especial attention has also been paid to decomposed tomato products, spoiled sardines, and wormy olives. Mineral waters have been frequently examined for pollution. Many misbranded medicines have been detained until the misbranding was corrected. Many shipments of low-grade alimentary pastes coloured in simulation of high grade products have been excluded.

Collaboration.

For other bureaus of the department 8194 samples were analysed. For other executive departments and Government establishments 789 were analysed as shown in detail in Table II. The totals do not include samples that were analysed by the field service of the Bureau. These are included among the miscellaneous samples given in Table I.

TABLE II.—Miscellaneous Analyses for other Branches of the Government.

Department of State	1
Department of the Treasury	65
Department of War	97
Department of Justice	3
Post Office Department	67
Department of the Navy	352
Department of the Interior	5
Department of Commerce	26
Department of Labour	1
Government Printing Office	10
The Panama Canal	90
District of Columbia	72
Total	789

Sixty-seven samples of fraudulent medicines sent through the mails have been analysed for the Post Office

Department. Assistance was also rendered at hearings and in court at trials.

Assistance was also given in the revision of the United States Pharmacopoeia and in the revision of the official methods of analysis of the Association of Official Agricultural Chemists.

DO EQUIATOMIC SOLUTIONS IN IRON POSSESS EQUAL RESISTANCES?*

By E. D. CAMPBELL (University of Michigan).

THE conception that carburized iron or steel is to be regarded as a solidified solution dates back as far as Proust in 1806, but the idea apparently remained dormant until 1863, when it was again suggested by Mathiessen. Since this latter date it has been more or less accepted by an increasing number of metallurgists and chemists, until at the present time it is almost universally acknowledged as being the most satisfactory theory to account for the properties of metals. That some intimate relation exists between the chemical composition of steel or other alloys and their electrical resistance was clearly pointed out in 1863 also by Mathiessen, and since that time the examination of this phenomenon has been the basis of many researches, such as those carried on by Johnson, Hopkinson, Osmond, Stead, Ebeling, Mathews, Hadfield, Benedicks, and Portevin. In 1898 Le Chatelier, in an article on the electrical resistance of steel (*Comptes Rendus*, 1898, cxxvii., 1709, 1782), drew four conclusions as the results of his investigations:—

1. The resistance increases with the percentage of carbon in the case of annealed steels.
2. For every 100 atoms of an alloy one atom of silicon increases the resistance by 7 microhms; one atom of manganese increases the resistance by 5 microhms, and one atom of nickel by 3 to 5 microhms.
3. Chromium, tungsten, and molybdenum have but slight influence on the resistance.
4. One atom of hardening carbon produces an increase in the resistance, practically equal to that of silicon.

Although Le Chatelier's work indicated that equiatomic concentrations of carbon as hardening carbon and silicon exerted practically equal effect on the specific resistance, while that due to manganese was only about five-sevenths as great, that of nickel three-sevenths to five-sevenths as great, and that due to chromium, tungsten, and molybdenum was very slight, Benedicks, in 1902 (*Zett. Phys. Chem.*, 1902, xl., 545), from the results of measurements made on seven steels in both the hardened and annealed condition, laid down the general law that equiatomic solid solutions in iron possess equal resistances. The formula which Benedicks proposed as the result of the study of his data was:— $\rho = 7.6 + 26.8 \Sigma C$ microhms cc.; in which ρ is the electrical resistance of the steel, 7.6 the electrical resistance of pure iron, and ΣC is the sum of the values in terms of carbon of the elements dissolved in the iron. The "carbon value" is obtained by dividing the percentage found on chemical analysis by the atomic weight of the element and multiplying the result by 12, the atomic weight of carbon.

No claim is made by Benedicks that the general law holds if the total carbon value exceeds 2 or at the outside 3 per cent. In an exhaustive study of the "General Considerations regarding the Electrical Resistance of Steels" (Iron and Steel Institute, *Carnegie Scholarship Memoirs*, 1909, l., 383), Portevin makes the following statement in regard to Benedicks' formula:—

"An attempt was made to verify this formula in the case of the steels which were employed for the shearing tests, the analyses of which have already been given in the first part of this report. The results of the calculation

* A Paper read before the Faraday Society, December 18, 1916.

tions are not recorded for the steels with low percentages of the special elements. Sometimes they agreed with the law, and at others the results were very far removed from the calculated resistances."

In order to develop a formula which would give calculated results in close agreement with those obtained experimentally, it was necessary for Benedicks to make two assumptions:—First, that the specific resistance of the pure iron solvent was 7.6 microhms, and, second, that steels with more than 0.45 per cent carbon retained 0.27 per cent in solid solution even when annealed, but that steels containing less than 0.45 per cent retained only between 0.06 and 0.07 per cent in solution after slow cooling. The carefully conducted experiments carried on during the past twenty years by J. O. Arnold, in which from 95 per cent to the entire amount of carbon in annealed steels has been recovered in the form of precipitated carbides, which tend to disprove the assumption that steels containing more than 0.45 per cent would retain 0.27 per cent carbon in solid solution.

The principal object of the experimental work herein described, which was carried on by Walter E. Jominy, M.Sc., has been to see whether it might not be possible to suggest a more satisfactory hypothesis to explain the relation existing between the carbon concentration and specific resistance of heat-treated steels than is offered by Benedicks' law.

The seven steels, which were furnished through the courtesy of the Pennsylvania, the Halcomb, and the Carpenter Steel Companies, consisted of one very pure basic open-hearth steel, three hypoeutectoid steels, and three which did not differ much from the eutectoid composition, one being somewhat below and the highest somewhat above the eutectoid point. The complete analyses of these steels, together with the carbon value of elements other than carbon, and the total carbon value, ΣC , are given in Table I.

Bars of the above steels, a little more than 6 mm. square and 15 cm. in length, were suspended in an electrically heated furnace, so arranged that the temperature could be accurately measured by means of a platinum-rhodium thermo-element, and oxidation of the bars during the time they were in the furnace could be completely avoided. When the furnace had been brought to the temperature from which it was desired to quench the bars, these latter were put in the furnace and allowed to remain one hour, in order to attain the exact temperature indicated by the thermo-element, which was placed within 2 or 3 mm. of the steels. The first four steels were quenched from 908° C. and the last three from 903° C. The time, taken with a stop-watch, required to transfer a bar from a furnace to a large body of ice-water used as quenching bath averaged about one second; while that required by the bar to cool below red-heat was from four-fifths of a second to one second. From five to six seconds were required to cool the bar to the temperature of the bath. After being hardened in this way the bars were polished, and the specific resistance was determined, the measurements being made on each bar immersed in an oil-bath maintained at 25° C. The specific resistances were determined by measuring the fall in potential between knife edges clamped to the bar 10 cm. apart, while a current of constant density was flowing through the bar. The fall of potential was compared with that given by a standard resistance which had been calibrated by means of a Siemens and Halske potentiometer and a certified standard cell. Measurements could be easily duplicated to within less than 0.05 microhms. and it is thought that the values given do not differ more than 0.2 of a microhm from their absolute value.

After measurements of the specific resistance of the quenched bars had been made, the bars were placed in a drying oven maintained at a temperature of about 105° C. for two days. This enabled the measurements, which were made at 95° C., to be made without appreciable change during the time of measurement. The bars were

finally carefully annealed by heating up to 880° C. and allowing to cool very slowly in the furnace over night.

The specific resistances of the bars in both the hardened and annealed conditions, together with the theoretical values calculated from Benedicks' formula, and the deviations of the value actually determined from those calculated, are given in Table II. In this same table the next to the last column shows the drop in the specific resistance due to the precipitation of carbides produced by annealing; while the last column gives the theoretical change in specific resistance which would be produced by the precipitation of 1 per cent of carbon, assuming the precipitation to be complete. If the molecular weight of the carbides decreases as the per cent of carbon increases, as was shown to be the case from a study of the products of solution of steel in 1899 (*Journ. Iron and Steel Inst.*, lvi., 223), since the carbides of low molecular weight are more readily soluble than those of high molecular weight, the progressive increase of effect on specific resistance for unit concentration of carbon with increasing carbon content of the steel, as shown in the last column of Table II., would be even more accentuated than the figures show.

For purposes of studying, the steels given in Table II. can be best divided into two groups of three each, beside the one steel, CO_4 ; the first, or hypoeutectoid, group consisting of H_{35} , H_{41} , and H_{57} ; and the second, or eutectoid group, consisting of C_4 , C_5 , and C_7 .

The marked deviations of the values found from those calculated from Benedicks' formula may be considered as follows:—

For steel CO_4 the formula gives a value of 9.63 microhms, a figure probably lower than that which has been obtained experimentally from the purest iron ever measured. The calculated values for H_{35} and H_{41} annealed are also lower than those experimentally found, since in these two cases the assumption is made that 0.07 per cent of carbon remains in solid solution, but the specific resistance due to this amount would not be sufficient to offset the low specific resistance, 7.6 microhms, assumed to be that of pure iron. According to Benedicks' formula 0.27 per cent of carbon would be equivalent to 7.24 microhms, and the further assumption is made that in annealed steels all those containing more than 0.45 per cent carbon retain 0.27 per cent in solid solution. The 7.24 microhms, due to the assumed 0.27 per cent carbon remaining in solid solution, would more than offset the low specific resistance assumed for pure iron; and, in consequence, we find the calculated value for H_{57} annealed 2.94 microhms higher than that actually found by experiment. This deviation from the calculated value decreases with increasing per cent of carbon, as might be expected, since, as has been pointed out before, the mean molecular weight of the carbides decreases as the per cent of carbon increases; and since the carbides of low molecular weight are more readily soluble than those of high molecular weight, the amount retained in solid solution in annealed metal would be reasonably expected to increase with increasing per cent of carbon, so that by the time the steel C_7 is reached, the observed value approaches quite near that calculated.

In the case of the hardened steels the calculated specific resistances are too high in the hypoeutectoid group, the deviation increasing from H_{35} to H_{57} . In the eutectoid group the calculated values approach much more nearly those found experimentally. The calculated value of C_4 is only 0.80 microhm too high, while the values of C_5 and C_7 are both below those found by calculation. All the deviations of the hardened steels cannot be satisfactorily explained by any hypothesis which assumes that equiatomic concentrations of carbon produce equal effect on the specific resistance.

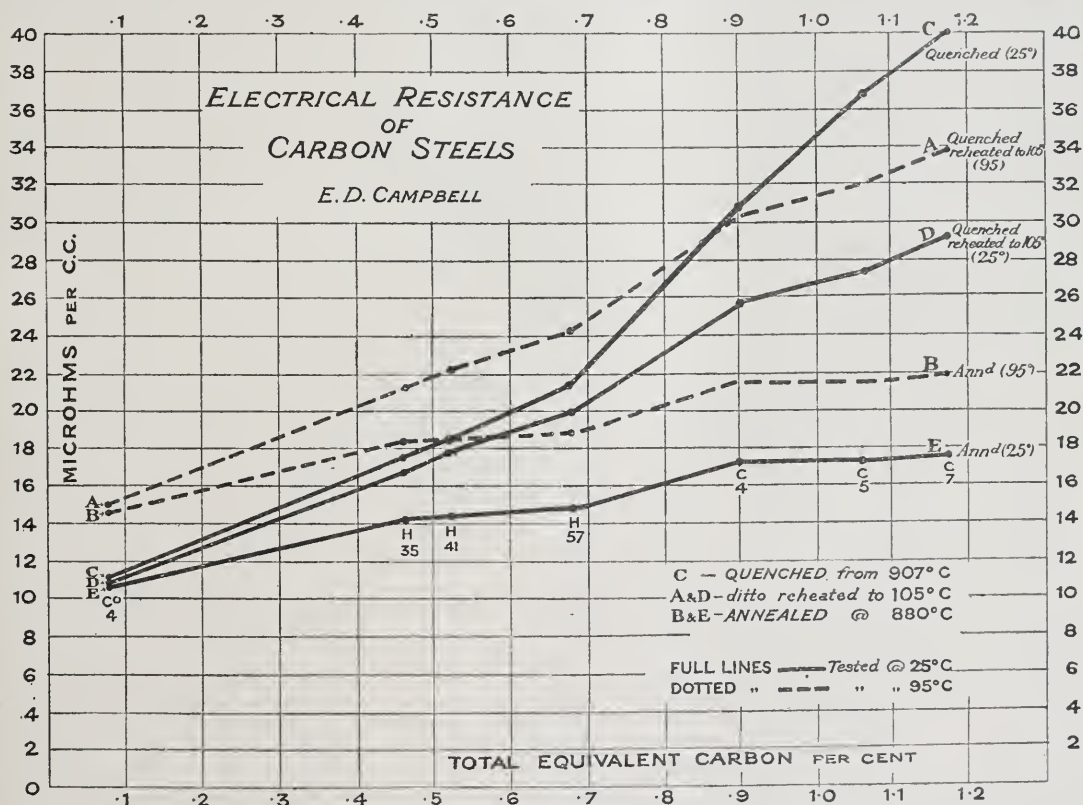
In the eutectoid group, in going from C_4 to C_7 , it will be noted that an increase of 0.29 per cent of carbon has produced an increase of 9.12 microhms in the total specific resistance. This figure, calculated to a basis of one atom of carbon to 100 of the alloy, would give a value of 6.73 microhms, which is in very satisfactory agreement with

TABLE I.

Steel.	Carbon per cent.	Manganese, per cent.	Phosphorus, per cent.	Sulphur, per cent.	Silicon, per cent.	Carbon value of elements other than carbon.	Total carbon Σ C.
CO ₄	0.04	0.10	0.007	0.029	—	0.036	0.076
H ₃₅	0.35	0.08	0.009	0.024	0.18	0.111	0.461
H ₄₁	0.41	0.08	0.012	0.016	0.19	0.111	0.521
H ₅₇	0.57	0.11	0.010	0.020	0.17	0.108	0.678
C ₄	0.76	0.221	0.016	0.041	0.169	0.141	0.901
C ₅	0.945	0.189	0.013	0.016	0.155	0.118	1.063
C ₇	1.05	0.190	0.013	0.020	0.167	0.124	1.174

TABLE II.

Steel.	Total carbon value Σ C.	Specific resistance of hardened steel.			Specific resistance of annealed steel.			Drop in sp. res. from hardened to annealed.	Drop divided by carbon per cent.
		Calculated from Benedicks' formula.	Found at 25° C.	Deviation from calcu- lated value.	Calculated from Benedicks' formula.	Found at 25° C.	Deviation from calcu- lated value.		
CO ₄	0.076	9.63	11.10	1.47	9.63	10.66	1.03	0.44	1.0
H ₃₅	0.461	19.96	17.63	2.36	12.45	14.38	1.93	3.25	9.3
H ₄₁	0.521	21.56	18.46	3.10	12.45	14.45	2.00	4.01	9.8
H ₅₇	0.678	25.78	21.41	4.37	17.72	14.78	2.94	6.63	11.6
C ₄	0.901	31.75	30.95	0.80	18.61	17.26	1.35	13.69	18.0
C ₅	1.063	36.09	36.82	0.73	18.00	17.23	0.77	19.59	20.7
C ₇	1.174	39.06	40.07	1.01	18.16	17.50	0.66	22.57	21.5



that of practically 7 microhms given by Le Chatelier as the value of one atom of hardening carbon in 100 of alloy. The value 6.73 microhms was obtained from steels quenched from 903° C., but experiments carried on in this laboratory have shown that if the quenching temperature had approached 1100° C., this value would have exceeded 8 microhms, on account of the lowering of the molecular weight of the dissolved carbides with the increased temperature. On the other hand, in the hypoeutectoid group, in going from H₃₅ to H₅₇, it will be noted that an increase

of 0.22 per cent carbon has produced an increase of 3.78 microhms in the total specific resistance. This figure, calculated to a basis of one atom of carbon to 100 of the alloy, would give a value of 3.68 microhms, which is not much more than one-half of the value obtained by an equal atomic concentration of carbon in the form of the carbides found in the eutectoid steels.

The values 6.73 and 3.68 microhms, for two equiatomic concentrations of carbon but in different groups of steels, show very clearly that some other explanation than

atomic concentration is necessary to account for these differences.

Although metallurgical chemists are accustomed to speak of steel and other alloys as solid solutions, they are not always in the habit of considering the mechanism of such solutions as being essentially the same as that of aqueous or other liquid solutions. In the analysis of metallurgical material the results are reported in per cents of the elements found, and, in consequence, most metallurgical chemists have formed the habit of thinking in terms of atoms of the individual elements rather than in terms of the molecules of the compounds of which these atoms form constituent parts. In the chemistry of ordinary solutions it is the molecule and not the atom that is the ordinary unit of thought. In studying influence of solutes on the properties of solutions it is customary to express the concentration of solutions in terms of molecules of the solutes and not in terms of the atoms of the elements which enter into the composition of the molecules. If, then, the essential unity of mechanism of metallic and of aqueous solutions is really accepted, and the molecule rather than the atom be taken as the unit of thought in studying such solutions, we may find in the last column of Table II. a suggestion for a possible explanation for the different amounts of influence produced on the specific resistance of steel by equiatomic concentrations of carbon. In this last column of Table II. are given the number of microhms resistance which would be produced by equal atomic concentrations of carbon existing in the form of the carbides found in the different steels. An examination of these figures shows that the effect of a given atomic concentration increases progressively as the carbon content increases from 9.3 microhms for the H₃₅, to 21.5 microhms for the C₇. These figures would suggest very strongly the idea that it is the molecular concentration of the carbides in solid solution and not the atomic concentration of the carbon which determines the extent of influence on the specific resistance exerted by such solutes. We would, therefore, propose to substitute for the statement that equiatomic concentrations in iron possess equal resistance, the hypothesis that equimolecular concentrations of carbides in solution exert equal influence

element in question in the molecule, and the atomic weight that of the element in question.

If the number of carbon atoms to the molecule of the carbides in one of the hardened steels were known, the assumption that equimolecular concentration of carbides exerts equal effect on the specific resistance would offer an experimental method for determining the molecular weight of the carbides in the other samples.

Benedicks' assumption that the total specific resistance of steel is made up of two components—that due to the solvent and that due to the solutes—seems to be based on sound experimental evidence which may be perhaps still further strengthened by the data given in Table III., in which are shown the specific resistances of the same steels used in the foregoing work, the specific resistance measurements being made at 25° C. and at 95° C.

The one striking point to be noted in these results is the almost constant value of the absolute increase in specific resistance with increased temperature, at which the specific resistance is measured, this increase differing very slightly from that of pure iron. These results would indicate almost beyond a question that the increase in specific resistance with increased temperature of measurement is practically wholly due to the increase in specific resistance of the solvent, while that component of the total specific resistance due to the solutes in solid solution is very slightly, if at all, affected by the temperature at which the specific measurements are made.

NOTES AND QUERIES.

* Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Food and Drugs Analyst.—I should be very grateful if some correspondent would outline in the CHEMICAL NEWS the best course to be pursued by a boy who wishes to become a food and drugs analyst.—F. J. FULLER.

MEETINGS FOR THE WEEK.

MONDAY, 29th.—Royal Society of Arts, 4.30. (Cantor Lecture). Town Planning and Civic Architecture," by Prof. Beresford Pite.

TUESDAY, 30th.—Royal Institution, 3. "The Old Brain and the New Brain, and their Meaning," by Prof. C. S. Sherrington.

— Royal Society of Arts, 4.30. "Imperial Industries after the War," by O. C. Beale. "The Work of the Y.M.C.A. in France," by Miss Ella C. Sykes.

THURSDAY, Feb. 1st.—Royal Institution, 3. "The Mechanism of Chemical Change," by Prof. F. G. Donnan.

— Royal Society. "Application of the Theory of Probabilities to the Study of a priori Pathometry," by Sir Ronald Ross and Miss H. P. Hudson. "Investigation into the Periodicity of Measles Epidemics in London from 1703 to the Present Day by the Method of the Periodogram," by J. Brownlee. "The Causes responsible for the Developmental Progress of the Mammary Glands in the Rabbit during the latter part of Pregnancy," by Capt. J. Hammond. "Post oestrous Changes occurring in the Generative Organs and Mammary Glands of the Non-pregnant Dog," by F. H. A. Marshall and E. T. Hulan.

— Chemical Society, 8. "Chromium Phosphate," by A. F. Joseph and W. N. Rae. "Detection of Traces of Mercury Salts in Toxicological Work," by K. C. Browning. "Stepped Ignition," by R. V. Wheeler. "Catalytic Bleaching of Oils, Fats, and Waxes," by H. Rai. "Alkaloidal Derivatives of Mercuric Nitrite," by P. C. Rây. "Synthesis of a Derivative of the Lowermost Homologue of Thiophene," by P. C. Rây and M. L. Dey. "Detergent Action of Soap," by S. U. Pickering. "Occlusion of Iron by the Phosphomolybdate Precipitate," by E. H. Archibald and H. B. Keegan.

FRIDAY, 2nd.—Royal Institution, 5.30. "The Supply of Gaseous Energy," by Dr. C. Carpenter.

SATURDAY, 3rd.—Royal Institution, 3. "Line in Plain Chant and Folk Song," by H. Walford Davies, Mus. Doc.

TABLE III.

Heat Treatment.—Quenched from 907° C.; tempered at 105° C.; annealed from 880° C.

Metal.	Carbon per cent.	Sp. res. at 25° C.	Sp. res. at 95° C.	Increase in sp. res.	Increase per degree.
CO ₄	0.04	10.90	15.11	4.21	0.060
		10.66	14.65	3.99	0.057
H ₃₅	0.35	16.83	21.14	4.31	0.062
		14.38	18.42	4.04	0.058
H ₄₁	0.41	17.89	22.25	4.36	0.062
		14.45	18.48	4.03	0.058
H ₅₇	0.57	19.87	24.23	4.36	0.062
		14.78	18.82	4.04	0.058
C ₄	0.76	25.75	30.35	4.60	0.066
		17.26	21.51	4.25	0.061
C ₅	0.945	27.31	31.98	4.67	0.067
		17.23	21.51	4.28	0.061
C ₇	1.05	29.19	33.83	4.64	0.066
		17.56	21.82	4.26	0.061

on the specific resistance. It is well known that different solutes of the same molecular concentration are dissociated to different extents and consequently influence the conductivity to a different degree, so that, until further evidence is forthcoming, a statement that equimolecular concentrations of all solutes in solid solution in iron exert equal effect on the specific resistance would not be justified. The molecular concentrations of solid solutions may be readily calculated from the formula $\frac{100d}{n \times \text{at. wt.}}$, in

which d is the density of the steel, a the element in question expressed in per cent., n the number of atoms of the

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ON THE RATES OF SOLUTION OF METALS IN FERRIC SALTS AND IN CHROMIC ACID.*

By R. G. VAN NAME and D. U. HILL.

(Concluded from p. 43).

GENERAL DISCUSSION OF RESULTS.

A SUMMARY of the reaction velocities in chromic acid is given in Table XI. Comparison with the results obtained in ferric sulphate, as summarised in Table VIII., shows a marked similarity between the two series, although chromic acid always gives higher velocities than ferric sulphate under like conditions. The chief points of similarity are the following:—

(a) In each series there is an approximate agreement, in the presence of 5 molar sulphuric acid, between the values for cadmium, nickel, tin, and copper, the differences being

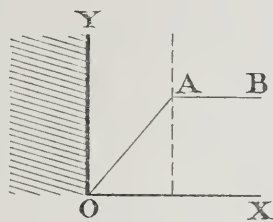


Fig. 1.

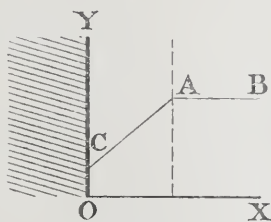


Fig. 2.

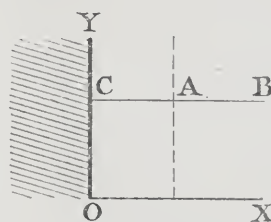


Fig. 3.

either within the experimental error or, at most, exceeding it but slightly.

(b) The values for silver are in all cases decidedly lower than for the other metals under like conditions.

(c) The agreement between different metals tends to become closer the higher the acidity.

TABLE XI.—Summary of Velocity Constants.—Chromic Acid.

	Molar concentration of H_2SO_4 .		
	0.25.	1.25.	5.
Cadmium ..	7.02	5.32	2.67
Nickel ..	Irregular	Irregular	2.67
Tin ..	—	—	2.74
Copper ..	6.95	5.34	2.72
Silver ..	4.28	—	1.22

Slight deviations from (c) appear in several cases, but are generally smaller than the experimental error, the only clear exception being the one which occurs with silver in chromic acid, due to the unexpectedly low value 1.22. This exception will be discussed on a later page.

Following the point of view explained on page 29, the observed reaction velocity is to be regarded as the resultant of the rates of two different simultaneous processes, the diffusion and the chemical reaction. The agreement between different metals in the strongly acid solutions indicates a nearly or wholly complete dependence, under these conditions, of the observed rate upon that of the diffusion process. On the other hand, the systematic differences which appear between the rates for different metals in the less strongly acid solutions show clearly

that in these cases the diffusion process is not the sole controlling factor, and point to the conclusion that the chemical reaction is here slow enough to have a specific influence upon the observed result. Especially significant in support of this inference is the fact that the sequence of the metals, when arranged in the order of their observed reaction velocities, is very nearly the same as that of the electromotive series, the agreement being as close as could be expected when due allowance is made both for the normal error of experiment and for the additional uncertainty which attaches to several of the values on account of specific complications already described.

So far, our explanation is well supported by the results. One important point, however, remains to be considered. It has been shown that the reaction velocity in all normal cases obeys the equation for a reaction of the first order, thus proving that the rate is proportional at every instant to the concentration of the oxidising agent. According to the view of Nernst this is due to the high velocity of the chemical reaction, which keeps the concentration of the oxidiser at the surface of the metal at practically zero. The observed reaction velocity is then the rate at which the oxidiser is supplied by diffusion, and this in turn is proportional to the difference in concentration between the two sides of the diffusion layer, which by hypothesis is equal to the concentration in the main body of the

solution. It is evident that this explanation holds only when the velocity of the chemical reaction is very great compared with that of the diffusion process, a condition which Nernst assumes to be always fulfilled except when secondary effects interfere.

Such a case, as Brunner (*Zeit. Phys. Chem.*, 1904, xlvii., 68) has shown, may conveniently be represented by a diagram, Fig. 1, in which the abscissæ represent distances from the surface of the metal, and the ordinates concentrations. The shaded portion is the metal, OY its surface, the dotted line is the outer limit of the diffusion layer, and the broken line OAB the concentration of the oxidiser at different points.

In the case of our results this explanation is applicable only to those experiments in the strongly acid solutions, in which, within certain limits, the reaction velocity is independent of the nature of the metal. Under conditions where different metals show different specific velocities (exemplified by the experiments at the lower acidities), the above explanation can not apply, yet we find that in general the reaction velocity in such experiments obeys the expression for a reaction of the first order quite as well as when the velocity is independent of the metal.

The point of view which we have adopted assumes that the influence of the metal manifests itself in such cases because the chemical reaction is not sufficiently rapid in comparison with the diffusion process. In other words, the concentration of the oxidising agent at the surface of the metal is not zero but has at every instant a finite value determined by the relative velocities of the two consecutive reactions involved. How this state of affairs can be reconciled with the observed obedience to the laws of a monomolecular reaction is a point which calls for explanation.

The case with which we are dealing, represented on a diagram of the same type as Fig. 1, gives Fig. 2, in which the ordinate OC represents the concentration at the surface of the metal. Similarly Fig. 3 shows the possible case of a reaction whose chemical stage is extremely slow in comparison with the diffusion stage, thus giving a concentration at the surface of the metal which is not sensibly different from that in the solution. The possibilities represented by these three figures will be hereafter referred to as Cases I., II., and III. respectively.

For Case I., Nernst's explanation, given above, is sufficient to account for the fact that the reaction velocity obeys the equation for a monomolecular reaction. In Cases II. and III., however, there is a finite concentration of the reagent at the surface of the metal. This can only occur when a part (in Case III., nearly all) of the molecules of the reagent which strike the surface of the solid phase fail to react with it, and hence remain in the solution. Now the frequency of the impacts will be proportional to the concentration of the reagent in the layer of liquid immediately adjacent to the solid, and the percentage of such impacts which result in reaction will, in a given case, be practically constant, independent of that concentration. It follows, therefore, that the rate of the chemical stage of the reaction will always be proportional to the concentration of the oxidising agent in the layer of liquid which is in contact with the solid, that is, the concentration at the inner surface of the diffusion layer.

Our results seem to furnish no example of Case III., but it is clear that here, just as in Case I., the rate would be proportional to the concentration of the solution, for this is the same as the concentration at the surface of the solid, which, in turn, determines the rate.

It only remains to be explained why Case II. shows the same behaviour. (Case II. is evidently the general one, I. and III. being merely limiting cases). As we have already shown that the rate must be proportional to the concentration at the surface of the metal, the problem resolves itself into proving that the concentration at the surface of the metal is proportional at every instant to the concentration in the solution. It is a simple matter to show that this is necessarily true except during a preliminary period of extremely short duration.

Let C_m represent the concentration of the oxidiser at the surface of the metal, and C_s its concentration in the solution. Further, let dm_1 be the weight of the oxidiser diffusing to the metal during the time interval dt , and dm_2 the weight used up during time dt .

The rate of the diffusion process is proportional to the difference in concentration on opposite sides of the diffusion layer. Hence—

$$dm_1/dt = K_1(C_s - C_m),$$

and since the rate of the chemical reaction proper is proportional to C_m —

$$dm_2/dt = K_2 C_m.$$

Since a preponderance of either process tends to retard it and to accelerate the other, it follows that a condition must sooner or later establish itself in which the rate at which the oxidiser is supplied is practically equal to that at which it is used up. Moreover, owing to the exceedingly small volume of the diffusion layer compared with that of the whole solution, this balance will be established almost instantly. Thereafter we can set, without any appreciable error,—

$$K_1(C_s - C_m) = K_2 C_m,$$

whence—

$$\frac{C_s}{C_m} = \frac{K_1 + K_2}{K_1}, \text{ a constant.}$$

That is, the concentration at the surface of the metal is proportional to that in the solution, which was to be proved.

The same reasoning must evidently hold for any reaction between a solid phase and a dissolved reagent,

provided, of course, that the case is not complicated by secondary interfering effects, such as the formation of an insoluble product, or the occurrence of further chemical reactions in the solution. We may therefore conclude that *obedience to the equation for a reaction of the first order is to be expected in all normal cases of this type, quite irrespective of the relative rates of the diffusion process and the chemical reaction proper.* This feature of our experimental results is thus fully explained.

In the discussion of our results we have employed a hypothesis which is neither a part of the diffusion theory nor a necessary consequence of it, namely, the assumption that an increase in acidity tends to accelerate the chemical stage of the reaction. This may or may not be true in general, but seems to apply here, for the mutual relation of the velocities recorded in Tables VIII. and XI. (barring minor differences explainable by experimental error) is in qualitative agreement with what would be expected if increasing acidity accelerated the chemical reaction, the effect of increasing viscosity being to retard the diffusion process, as we have already seen.

Only one value, the one referred to above as exceptional, fails to conform to this explanation. This is the velocity for silver in chromic acid in the presence of 5 molar sulphuric acid, which is unexpectedly low, as the following comparison shows:—In ferric sulphate the ratio $Cd : Ag$, as would be expected, is lower in 5 molar than in 0.25 molar acid (1.42 and 2.48 respectively). In chromic acid, on the contrary, the corresponding ratios are 2.19 and 1.64, thus showing that the higher acidity has here failed to bring silver into closer agreement with the other metals.

We must not overlook the fact that from the standpoint of the diffusion theory alone there is no reason for regarding this particular value as anomalous. It becomes so only when considered in the light of that theory combined with our assumption concerning the effect of acidity upon the velocity of the chemical stage of the reaction. Whether this result is to be regarded as an exception to the rule assumed, or is, rather, to be ascribed to the effect of some unknown disturbing factor, is a question which can hardly be settled without more experimental evidence.

The Influence of Adsorption.

In discussing our experimental results we have thus far taken no account of the possible influence of adsorption effects. A supplementary hypothesis based on adsorption will now be briefly considered. It does not alter or supersede any of our previous conclusions, but is offered in order to show that a conception of the mechanism of heterogeneous reactions based on adsorption is not incompatible with the diffusion theory, but rather supplements it.

Our solutions contained in all cases free acid, usually in relatively large proportion, amounting in some instances to several hundred times the concentration of the oxidising agent itself. Let us assume that the metal is covered by an adsorbed layer of molecules of sulphuric acid. Similar relations are to be understood for the hydrochloric acid used in the experiments with ferric chloride. Following the point of view suggested by Langmuir (*Journ. Am. Chem. Soc.*, 1916, xxxviii., 1147), we may imagine these acid molecules to form a layer, one molecule deep, in chemical combination with the outer layer of atoms of the metal, which by virtue of their position possess residual combining power. Since the hydrogen of the acid molecules will be virtually competing with the metal for the negative radical of the acid, this hydrogen will be rather loosely combined, and will undergo oxidation very readily.

The fraction of the whole number of what Langmuir calls "elementary spaces" so covered by adsorbed molecules will depend upon their concentration in the solution and upon the nature of the metal, and is probably greater the more easily oxidisable, *i.e.*, the more electropositive

the metal. When this fraction is near unity the surface of the solid will practically consist of readily oxidisable hydrogen atoms which undergo immediate oxidation on suitable contact with a molecule of the oxidiser, so that the latter will be used up at the surface of the solid as fast as supplied by diffusion. This explains Case I. When the fraction is below unity the surface is only partly covered and some accumulation of the oxidiser at the surface results, the molecules which do not encounter active hydrogen on contact with the solid reacting slower or not at all. This gives Case II., or, in the limit, Case III. The oxidation of the hydrogen of an adsorbed acid molecule is followed by the prompt escape into the liquid of the molecule of metallic sulphate or chloride so formed, since owing to the low concentration of that kind of molecules in the liquid they would be less strongly adsorbed than the acid molecules.

The fact that in Case II. the observed reaction velocities for different metals follow the same order as the electromotive series can be ascribed either to the dependence of the amount of adsorption upon the electromotive behaviour of the metal (see above), or to the influence of the secondary reaction, that is, the one which results when a molecule of the oxidiser finds its way into direct contact with the metal. This reaction may reasonably be assumed to be more rapid the more electropositive the metal.

The view that the velocity of the chemical reaction increases with the acidity, which we found it expedient to adopt in the general discussion of our results, would evidently be a necessary consequence of this adsorption hypothesis. Finally, since this hypothesis involves nothing to limit or alter the rôle of diffusion, the explanation, from the present point of view, of those phenomena which we have ascribed to the influence of diffusion calls for no change.

In short, it makes little difference here, in employing the diffusion theory, whether we consider the case from the standpoint of adsorption or not. In general, however, the combination of the two points of view should lead us farther than either one alone.

Status of the Diffusion Theory. Normal and Abnormal Cases.

An important result of this investigation is the proof of the existence of cases in which we are almost inevitably led to the conclusion that the reaction at the boundary surface is one of limited velocity. Opinions may differ as to whether these cases represent real or only apparent exceptions to Nernst's hypothesis that the attainment of equilibrium at the boundary surface between two phases is practically instantaneous. It is after all largely a matter of definitions. The practical bearing of these cases, however, is obvious. They show that we can not assume, as an over-strict interpretation of Nernst's view-point might lead us to do, that every case in which different solids react at different rates with the same dissolved substance can be ascribed to some tangible and experimentally demonstrable interfering effect. (If, however, the solid is somewhat soluble in the pure solvent we are really dealing with a two-stage reaction, and agreement between the rates for different solids would not necessarily be expected, even when the second stage is instantaneous. Example: Solution of different slightly soluble acids in the same dissolved base.) If the cases in point are due to secondary interference it must be interference of a sort which only Maxwell's demon could recognise as not being a normal part of the mechanism of a reaction of the given type. In order to avoid such fine and elusive distinctions it is much better to admit the existence of phenomena which may or may not be theoretically equivalent, but are certainly practically equivalent, to a limited reaction velocity at the actual boundary surface.

What, then, is the status of the diffusion theory? It is evident that by this modification the diffusion theory loses

a good deal of its simplicity and beauty, but its usefulness is not seriously impaired. We must now admit, as strictly normal, cases in which the influence of diffusion upon the observed rate of the reaction has any value between 100 per cent and zero. It may be that values close to 100 per cent will prove far more common in practice than lower ones, or, in other words, that Nernst's hypothesis is sustained much more often than it is contradicted, but its validity in a given case cannot always be assumed *a priori*.

Finally, in employing the diffusion theory we must be on our guard against cases in which the normal relation between diffusion and reaction velocity is disturbed by secondary interfering effects. Since it is desirable to be able to predict these exceptions in advance, a knowledge of the different known types, and of their specific effects upon the results, is important. The present investigation has furnished examples of four. These are:—

(a) Insolubility of one of the products of the reaction, with consequent formation of a coating on the solid phase.

(b) Occurrence of the reaction in two stages of which the second is of limited velocity and is not confined to the actual contact surface.

(c) Passivity.

(d) Evolution of a gas.

These four types seem to include all that have thus far been reported (Nernst, in his "Theoretical Chemistry," third English edition, p. 587, specifically mentions only the first two). Of these, passivity is indicated by a marked dependence of the initial reaction velocity upon the preliminary treatment of the metal, and a two-stage reaction can be detected either by analysis of the solution or by the abnormally small effect of variation in the rate of stirring upon the observed reaction velocity. (An interesting case of a two-stage reaction is that of arsenic trioxide when dissolving in water. After dissolving as As_2O_3 it undergoes hydration either in the solution or, possibly, as E. Brunner has suggested, wholly in the diffusion layer. This second stage is of course not detectable by chemical analysis. See Drucker, *Zeit. Phys. Chem.*, 1901, xxxvi., 201 and 693; L. Bruner and Toloczko, *Zeit. Anorg. Chem.*, 1903, xxxvii., 455; E. Brunner, *Zeit. Phys. Chem.*, 1905, li., 494). Insoluble or gaseous products will usually show their presence by visible effects. All of these types of interference are of such a nature that they could generally be predicted in advance.

Summary.

Measurements have been made of the rates at which different metals react with the same oxidising solution in the presence of varying concentrations of free acid. The solutions used were (a) ferric sulphate and sulphuric acid, (b) ferric chloride and hydrochloric acid, and (c) chromic acid and sulphuric acid. The chief experimental results are the following:—

1. When the acidity is sufficiently high, a number of metals give the same reaction velocity under like conditions, showing that diffusion is here the determining factor.

2. With decreasing acidity such agreement tends to disappear, and the observed velocities then depend upon the nature of the metal, the order being approximately the same as the electromotive series and the velocity greater the more electropositive the metal.

3. The rate of the reaction in normal cases is proportional to the concentration of the oxidising agent, not only under conditions where different metals give the same rate, but also where the rate depends upon the specific nature of the metal.

From these and related facts the following conclusions are drawn. They apply only to normal cases, that is, to those in which the progress of the reaction is not interfered with by mechanical effects, such as insoluble coatings and the like.

4. The velocity of a reaction at the actual boundary surface between a solid and a liquid is not necessarily extremely rapid, even when there is no mechanical interference with its progress.

5. When a solid reacts with a dissolved reagent and the reaction velocity at the boundary surface is limited, a balance is quickly established between the consumption and the supply (by diffusion) of the reagent, such that its concentration at the boundary, under otherwise constant conditions, is always proportional to its concentration in the solution.

6. The rate of the reaction at the boundary surface may in some cases be low enough, compared with the rate of the diffusion process, to be an important, or even the predominant factor in determining the observed reaction velocity. A sound interpretation of the diffusion theory must take account of this possibility, which has heretofore been neglected.

STUDIES ON THE ORIGIN OF MISSOURI CHERTS AND ZINC ORES.*

By G. H. COX, REGINALD S. DEAN, and
V. H. GOTTSCALK.

SOME GENERAL PROPERTIES OF COLLOIDS.

COLLOIDS have been so variously defined that no attempt will be made to give an exact definition, it being sufficient for the purpose in hand to consider a "sol" or "colloidal solution" a two-phase system in which one phase is very finely dispersed through the other, the dispersed phase being prevented from settling by intermolecular or electrical forces. A common example of this is the dispersion of SiO_2 in H_2O . Recent investigation tends to show that crystalline substances, as well as amorphous ones, form colloidal solutions (sols), providing the degree of subdivision be sufficiently great.

Water colloidal solutions (hydrosols) may be formed in a number of ways (see Svedberg, "Herstellung kolloidaler Lösungen Anorganisches Stoffe," Th. Steinkopf, Dresden, 1910). Some of these which are of particular interest in connection with geologic problems are—

1. *Chemical Method, applicable particularly to SiO_2 and Fe_2O_3 .*—Here the solution or sol, following Taylor's nomenclature, is formed by the decomposition of some other compound. Thus colloidal SiO_2 may be obtained by the hydrolysis of sodium silicate and colloidal Fe_2O_3 by the hydrolysis of FeCl_3 . This is the method by which colloidal silica is most commonly formed in nature.

2. *Method of Barzelius, applicable to Sulphides.*—The chemically precipitated substance (such as ZnS) is washed with pure water until all the electrolyte is washed out, after which it begins to solate. The only factors necessary are sufficient time and a large amount of water, both of which may be had in almost unlimited quantities in nature.

3. *Method of Spring, applicable to Sulphides.*—The precipitated substance is treated with a peptising or solating agent (some foreign substance which aids solution, e.g., H_2S), when it solates.

4. *Protective Colloid Method.*—The substance is treated with some substance which prevents it from being precipitated by electrolytes. Thus a hydrosol of PbS may be readily formed by passing H_2S into a gelatin sol containing $\text{Pb}(\text{NO}_3)_2$.

There are many other methods which may find application in nature, but most of them are modifications or combinations of the four given above. An example is the formation of a lead sulphide hydrosol by treating a kaolin suspension containing lead acetate with H_2S , in which case the kaolin and lead sulphide are precipitated as in

intimate mixture. On continued washing with water the lead sulphide is obtained as a hydrosol.

Another example is Bredig's electrical dispersion method ("Anorganische Fermente"; see also *Journ. Am. Chem. Soc.*, 1915), which, although it may not be of geologic importance, is an excellent laboratory method for the preparation of many colloids from natural crystals. It has recently been shown that this method is merely a way of finely dividing the substance by suddenly cooling its vapour. Further, Wigilin (*Journ. Am. Chem. Soc.*, 1914) has recently prepared colloids by finely grinding the substances in an agate mortar, a method which indicates that if a substance be sufficiently finely divided it may be taken into colloidal solution. We have prepared colloidal lead sulphide by suspending two crystals of galena in water and passing an electric current of fairly high voltage (in this case 220 volts direct current) between them.

Hydrosols are precipitated by electrolytes, negative colloids by the positive ions, and positive colloids by the negative ions—Hardy's rule (*Proc. Roy. Soc.*, 1899, lxi., 110). Colloids are also precipitated by other colloids of opposite sign, both being thrown down. As a rule the colloids of silica and the sulphides are negative and those of Fe_2O_3 and Al_2O_3 positive; but the sign of a colloid may vary with the nature of the medium. The readiness with which an electrolyte produces precipitation varies with the concentration and valence of the precipitating ion—H. Schulze's rule (*Journ. Prakt. Chemie*, 1882, xxv., 431).

Al ions are much more efficacious in precipitating silica from a hydrosol than are H ions. Probably the most important electrolyte taking part in the precipitation of colloids in nature is calcium bicarbonate, $\text{Ca}(\text{HCO}_3)_2$. When a colloid is precipitated by an electrolyte it carries down with it the adsorbed ion in the form of hydroxide or acid. Thus silica precipitated by $\text{Ca}(\text{HCO}_3)_2$ carries down with it a small amount of $\text{Ca}(\text{OH})_2$. The precipitation of one colloid by another of opposite sign probably finds its most common example in the precipitation of silica and sulphides by the colloids in clay.

Colloids are not in general precipitated in the crystalline state, but, according to van Bemmelen ("Die Absorption Gesammelte Abhandlungen über Kolloide und Absorption," Th. Steinkopf, Dresden, 1910) and von Veimann ("The Chemistry of Colloids," by W. W. Taylor), any colloid may be obtained in the crystalline state if the dilution and the interval of time be sufficiently great. Although these conditions cannot be obtained for silica in the laboratory, they can be readily obtained for more soluble substances, such as barium sulphate, and all stages of the transition between a gel and a crystalline substance can be prepared.

General.

Because of their common occurrence, wide distribution, economic importance, and close relations to a number of important ore deposits, cherts have been the object of considerable study. Chert is commonly defined as a cryptocrystalline aggregate of silica, and may be formed in a large number of ways. The silica itself may have been contributed directly from an igneous magma, it may have resulted from the weathering of silicate minerals, or it may have gone through an intermediate stage by deposition or by being taken to form the solid parts of organisms from which it later collected by solution or re-crystallisation. The arguments as to whether the silica has been derived from within or from without the formation in which the chert is developed still continues, but it seems safe to say that silica is derived from both sources, each being of major importance in certain cases.

So far as we are aware silica is transported only in the colloidal form (see Kahlenberg and Lincoln, *Journ. Phys. Chem.*, 1898, ii., 77). While it is somewhat common and convenient to speak of its transfer as sodium silicate, &c., this is, strictly speaking, inaccurate, as such compounds almost certainly dissociate to form colloidal silica.

After having been taken into solution there are also various ways in which deposits of chert may result (see F. W. Clarke, *Bull.* 491, p. 518, U.S. Geol. Survey, 1911). Griswold ("Report Arkansas Geol. Survey, 1890, iii.) considers the novaculite deposits of Arkansas to be a siliceous sediment, while others think that they are the result of a chemical precipitation or of the replacement of limestone by silica. Van Hise and Leith (*Mon.* 52, U.S. Geol. Survey, 1911) advance the theory that the great deposits of chert associated with the iron deposits of the Lake Superior region were formed largely by the precipitation of silica derived from magmatic sources, and to a less extent by the later alteration of greenalite, FeSiO_3 . Lawson ("Fifteenth Annual Report U.S. Geol. Survey," 1895, p. 193) believes that the radiolarian cherts of California are the result of precipitation of colloidal silica from submarine springs. Sollas (*Ann. and Mag. Nat. Hist.*, 1880, [5], vi., 384) describes cherts which he considers to have been formed by the re-crystallisation of the siliceous remains of organisms.

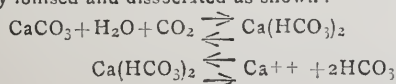
Many think that cherts are in the main the result of the replacement of limestone, and Church (*Journ. Chem. Soc.*, 1862, xv., 107) has shown experimentally that this can take place. Others have repeated the experiments made by Church, but no one appears to have offered an explanation for the change. There seems to be a general impression that nodular cherts and sometimes layers grow along lines of easiest relief, after the manner of true concretions, by replacing or by pushing the wall rock aside.

Cherts are generally of secondary origin, *i.e.*, later than the enclosing rock; but it is recognised that they are both epigenetic and syngenetic, and that each of these two types may result from different conditions. While this discussion will be found to be applicable in part to all cherts, it is concerned primarily with epigenetic cherts of the south-western Missouri zinc district.

The occurrence of silica in nature as hydrosol or colloidal silica has long been known (Köhlenberg and Lincoln (*Journ. Phys. Chem.*, 1898, ii., 77), and it is evident from the above that it has been used from time to time to explain the origin of certain siliceous rocks, especially cherts. Julien (*Proc. Am. Assoc. Adv. Sci.*, 1879, p. 398) has suggested that some of the silica may be carried in combination with humic acids, but there is little evidence to indicate that such transportation is important. Our analyses show that many shales and limestones contain as much as 1 per cent of SiO_2 soluble in dilute acids. Consequently, it is evident that silica does occur in nature as such. We shall start with this assumption.

From reading the literature on cherts one is apt to obtain the impression that their precipitation in limestones and shales has been largely the result of inoculation of siliceous solutions by the remains of siliceous organisms and quartz grains, or has resulted from a surface tension effect causing larger grains to grow at the expense of smaller ones. A perusal of the literature also leads to a belief that the deposition of amorphous and cryptocrystalline silica in openings has resulted from a vague tendency of colloidal silica to precipitate on standing. It appears to the writers that in all the reports that have been written, the most important explanation for the precipitation of silica, especially in connection with carbonate rocks, has been overlooked, and that there are many cases in which the occurrence of chert may be better explained by the application of some of the principles of colloidal chemistry as above outlined.

Colloidal silica in water is not precipitated by carbon dioxide because carbonic acid is a very poor electrolyte; *i.e.*, it undergoes very slight dissociation in water. But when water containing CO_2 comes into contact with carbonate rocks, ordinarily limestone, and dolomite, an acid carbonate is formed, which, like all salts, is more or less readily ionised and dissociated as shown:—



The positive calcium ions so formed are very efficient in precipitating colloidal silica, even more so than the small amount of hydrogen ions formed from the dissociation of carbonic acid, since the precipitating power increases with the valence—H. Schulze's rule (*Journ. Prak. Chem.*, 1882, xxv., 431; see also Hardy, *Journ. Phys. Chem.*, ii.; and Whitney and Over, *Journ. Am. Chem. Soc.*, 1903, xxiii., 252). It is possible that the precipitation of silica by the electrically opposite colloids in clay may be effective in some cases.

A colloidal silica solution prepared from water-glass and hydrochloric acid was purified by dialysis until free from chlorides. To test the effect of CaCO_3 on silica hydrosols and to determine if the reaction was due to the presence of CO_2 , two sets of solutions of colloidal silica were made up, one of which was freed from CO_2 and the other saturated with it. To both sets was added ground calcite, with the result that the set which was free of CO_2 is still stable after standing a year, while the one containing CO_2 precipitated completely within an hour.

(NOTE.—It is worthy of note that the CaCO_3 not only failed to precipitate the silica, but that it clearly acted as a peptising agent, as the silica in the original solution came down many months ago).

This shows conclusively that silica hydrosols will be precipitated by CaCO_3 in the presence of CO_2 , the two combining to form calcium bicarbonate, which is a good electrolyte and which dissociates or ionises. The precipitation is due to the electrolyte thus formed.

Several ordinary dolomites and calcareous shales were also tried, both in powdered form and as coarse fragments, all of which produced the same result as obtained with pure CaCO_3 . Doubtless if the solution were made very dilute and a long period of time allowed, small pieces of limestone could be silicified, as the silica appeared to be precipitated at the point where the CaCO_3 went into solution. This is probably the explanation of Church's experiment in which coral was silicified.

Much secondary chert has been ascribed to the replacement of limestone by silica, the chief evidence being the preservation of rock and fossil structures and textures, irregular contacts, and a gradual gradation from pure chert to pure limestone. By the application of the principles of the precipitation of colloids by electrolytes, this process can be placed upon a chemical basis and shown to be a true case of metasomatic replacement. The petrification or silicification of wood may thus result from the precipitation of the negative colloidal silica by the numerous positive humic colloids formed by the decay of the wood, and while both colloids would be thrown down together, the humic colloids would soon escape by further decomposition into CO_2 , H_2S , &c. Doubtless many other cases can be explained in this manner.

The partial crystallisation of colloidal silica to form chert may be explained according to Von Weimarn's theory, that the greater the dilution and the length of time the more crystalline the precipitate.

Much evidence that chert originated from a gel condition may be found in cherts themselves, the most common of which is the presence of shrinkage cracks. The jasperoid of South-west Missouri zinc district often shows a pronounced banding, which in part must be attributed to this cause. Bain has called attention to many shrinkage cracks and vugs in the cherts of that district which could have resulted only from the shrinkage of a gel.

If, then, cherts in sediments are largely epigenetic in origin, having resulted for the most part by the replacement of limestone by colloidal silica precipitated by electrolytes, generally carbonates, the solution of which has been brought about by the presence of CO_2 , it should follow that such cherts are indicative of the direct circulation of meteoric waters of low carbonate content at that point during the time of their formation. It therefore follows that their formation should be limited to depths of a few hundred feet; *i.e.*, they should, in general, be

formed but a short distance below the water table at the time of their disposition.

Description of Jasperoid of South-west Missouri.

This substance has been called quartzite by Schmidt, cherokee by Jenney, jasperite by Jenney and Shepard, secondary chert by Winslow and by Hawerth; later secondary chert by Bain, Van Hise, and Adams, and black chert by Buckley and Buchler, and jasperoid by Smith and Siebenthal, and by Siebenthal. The name jasperoid was given it by Smith and Siebenthal (Folio 148, U.S. Geol. Survey, 1907) because of its similarity to a gangue material found in the Aspen mining district of Colorado as described by Spurr (Vol. 31, U.S. Geol. Survey, 1898, p. 210). Siebenthal notes similar gangue material associated with the lead and zinc ores of Kentucky (U.S. Geol. Survey Bull. No. 606, 1915, p. 216). It is to be expected that such material will be found in many localities, as it differs from ordinary chert only in coarseness of grain, and in having been transported and precipitated with sulphide ores.

This substance is the most abundant gangue mineral accompanying the zinc ores, and, while it may occur in any of the deposits, is abundant in and characteristic of the deposit of the sheet-ground where it is found with the sulphides, cementing fragments of the Grand Falls chert. Fresh samples vary in colour from light grey to black, the dark variety being the more common. It is hard, dense, and tough; has a marked conchoidal fracture, and breaks into sharp angular fragments, as does an ordinary chert, although the fractured surface of the former is less smooth and the grain more coarse. It usually contains crystals and fragments of the sulphide mineral, especially sphalerite and galena, together with grey chert, dolomite, calcite, and other impurities of macroscopic, microscopic, and sub-microscopic sizes.

Microscopically it consists chiefly of a fine-grained xenomorphic aggregate of irregular rounded or wedge-shaped quartz grains, the diameter of which usually have a length of 0.02 to 0.06 mm. They are therefore properly excluded from the true chert family, whose structure is cryptocrystalline. While the grains tend to be rather uniform in size, a great deal of variation can be noted. In some cases the grains are interlocked by pronounced suture structures, but in others such structures are lacking. Some specimens contain abundant carbonate rhombs, usually dolomite, which may constitute as much as 20, or even 50 per cent of the mass, but other samples may show no carbonate at all. Scattered irregular cloud-like aggregates of what probably are kaolin and organic matter, together with sulphide crystals, may be abundant or practically absent. There seems to be no macroscopic or microscopic impurities that are present in all samples.

Jenney (Trans. Am. Inst. Min. Eng., 1894, xxii., 195) explains the origin of the jasperoid as follows:—

"Analyses and microscopic examination of samples of cherokee (jasperoid) show that this rock has been formed by the silicification of the residual sandy mud resulting from the dissolution of the Cherokee limestone by waters charged with carbonic acid."

Bain (Twenty-second Ann. Report U.S. Geol. Survey, 1901, Part 2, p. 107) recognised that the silica may have been precipitated in some manner as a colloid, by suggesting "that at the time the blende was formed the siliceous matrix was in a colloidal condition, . . ."

Smith (Folio 148, 1907, p. 14) does not say in what form the silica was precipitated, but believes that "the jasperoid is, in nearly all cases, the result of a metasomatic replacement of limestone."

Siebenthal (U.S. Geol. Survey Bull., 1915, No. 606, p. 183) qualifies Smith's statement by adding: ". . . the replacing silica may for a time have been in a colloidal state."

A recognition of the transportation of silica in the colloidal form, of the readiness with which it is precipitated on encountering carbonated waters in limestone, of the

suspended fragments of grey chert and crystals of sulphide minerals, both with and without crystal boundaries contained in the jasperoid, and of the evidence of abundant shrinkage openings, leads to the conclusion that the silica of the jasperoid was not only precipitated in the colloidal form, but that practically all of it also existed at the same time in the colloidal form, although in different stages of desiccation. Characteristic shrinkage cracks are common. Doubtless all traces of many of the cracks which were first to form have been lost, but many of these formed before the deposition of jasperoid had ceased are still to be recognised on polished surfaces by a slight difference in the filing material, the later jasperoid being, in general, lighter in colour.

Given a colloidal solution entering an underground drainage course in limestone and chert in which decomposition products have accumulated to a more or less extent, the introduction into it of an electrolyte, such as $\text{Ca}(\text{HCO}_3)_2$, might well result in all the conditions outlined by the above writers, so that it is quite probable that at some place each of these conditions may exist. However, the importance assigned by Smith and by Siebenthal to the process of forming jasperoid by the replacement of limestone seems to be too great. Much of the jasperoid occurs as a cement in brecciated areas in the Grand Falls chert, a fact which in itself precludes the possibility of this portion of it having been formed by the replacement of limestone.

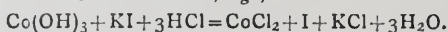
(To be continued).

A NEW VOLUMETRIC METHOD FOR THE DETERMINATION OF COBALT.

By W. D. ENGLE and R. G. GUSTAVSON.

As the quantitative determination of nickel and cobalt in the presence of one another is difficult, this investigation was undertaken to find, if possible, simpler methods than those commonly used. It was hoped that volumetric methods might be found whereby either of these metals might be easily determined in the presence of the other. A very satisfactory method for cobalt has been found, but in the case of nickel nothing better than the methods already in use has so far been discovered.

In the presence of sodium or potassium hydroxide both nickel and cobalt are oxidised to trivalent oxides or hydroxides by various oxidising agents, but neither trivalent nickel nor cobalt forms stable salts with acids. Both nickelic and cobaltic hydroxides, when treated with acids and potassium iodide, liberate iodine and form the nickelous or cobaltous salts, e.g.,—



Of these two metals, cobalt is the more easily oxidised, and when oxidised forms the more stable compounds. For example, cobalt sulphate treated with potassium hydroxide and hydrogen peroxide gives cobaltic hydroxide, while nickel under the same treatment is not changed even at the boiling point. A. Metz (Zeit. Anal. Chem., 1914, liii., 537) uses this fact as a basis for the determination of cobalt. The difficulty in completely removing the excess of hydrogen peroxide either by boiling or filtering and washing, is an objection to this method. After trial of a number of oxidising agents, sodium perborate proved to be the best, both because it completely oxidises the cobalt without affecting the nickel and also because any excess of the reagent is readily decomposed by boiling.

The method recommended is as follows:—The ore, or other material, may be dissolved with acids and the metals of the copper and iron groups and also manganese removed by standard methods. The solution so obtained may contain nickel and cobalt, zinc, and the metals of the alkalis and the alkaline earths, but must be free from any substances capable of liberating iodine from an acid solu-

tion of potassium iodide. This solution, with a volume of about 100 cc., is made acid with dilute sulphuric acid, using about 5 cc. in excess, and 1 or 2 grms. of dry sodium perborate added. After agitation and solution of the perborate, sodium hydroxide is added to strong alkaline reaction and the mixture boiled for ten minutes to decompose the excess of perborate. The solution is now cooled to room temperature and after 1 gm. potassium iodide has been added, acidified with dilute sulphuric acid. After solution of the precipitate, the liberated iodine is titrated with a standard solution of sodium thiosulphate, using starch paste as an indicator.

As it is difficult to secure a cobalt compound of known cobalt content, it is recommended that the sodium thiosulphate solution be standardised by means of potassium dichromate in the usual manner. Since $1K_2Cr_2O_7 = 6I = 6Co$, the $K_2Cr_2O_7$ factor of the thiosulphate solution multiplied by 1.2027 gives its cobalt factor.

If a cobalt compound of known purity is available it may be used to standardise the sodium thiosulphate solution by taking a weighed quantity and treating, as in the regular method, with sodium perborate and sodium hydroxide. After boiling for ten minutes, cool, add potassium iodide and acidify with dilute sulphuric acid; titrate the free iodine with the thiosulphate solution and compute its factor. By this method 0.1613 gm. of cobalt as cobalt sulphate required 35.23 cc. of the sodium thiosulphate solution, making its factor 0.004575 while its factor as determined by the potassium dichromate method was 0.004568.

The results of a few of the analyses of mixtures of cobalt and nickel are given in Table I. The cobalt used was a solution of pure cobalt sulphate containing 0.00978 gm. of cobalt per cc. The nickel used was a solution of nickel sulphate free from cobalt and contained 0.00908 gm. of nickel per cc. The titrations checked one another within a 0.1 cc. and wide variations in the amounts of the sulphuric acid, sodium perborate, &c., used did not affect the results. It may be noticed that the process is accurate for widely different amounts of cobalt and also in the presence of large quantities of nickel.

TABLE I.—Determination of Cobalt in the Presence of Nickel.

Expt. No.	Grm. nickel present	Grm. cobalt	
		Present.	Found.
1.	0.0454	—	—
2.	0.0908	—	—
3.	—	0.0489	0.0492
4.	—	0.0489	0.0487
5.	0.0908	0.0489	0.0490
6.	0.0454	0.0489	0.0491
7.	0.04540	0.0489	0.0491
8.	0.04540	0.0489	0.0495
9.	0.0908	0.0978	0.0977
10.	0.0908	0.0978	0.0982
11.	—	0.1467	0.1470
12.	0.0908	0.1467	0.1466
13.	—	0.1956	0.1950
14.	0.2270	0.1956	0.1955
15.	—	0.2445	0.2439

The following points in this analysis must be carefully observed to obtain accurate results:—It is necessary to add the sodium perborate to the acid solution and then make alkaline. Attempts to add the perborate to the alkaline solution resulted in incomplete oxidation of the cobalt when the amount present was more than 0.050 gm. It is necessary to add the potassium iodide before adding the dilute sulphuric acid for the solution of the cobaltic hydroxide, otherwise the results will be low. This method does not require the filtration of the cobaltic hydroxide, which is important not only in saving time, but in increasing the accuracy, as this compound tends to pass through the filter during the last part of the washing.

It was attempted to determine nickel and cobalt together by an analogous method using more powerful oxidising agents such as bromine water and sodium persulphate. These experiments were not successful, due to the difficulty of completely removing the excess of the oxidising agent. The nickelic and cobaltic hydroxides, which are readily formed, require filtration and excessive washing and even after prolonged washing the results were usually high. Cobalt free from nickel gave good results when oxidised with bromine water, but even here the washing required was excessive and the method is much inferior to the one given above using sodium perborate.

In conclusion we would state that cobalt may be determined in the presence of nickel by oxidation in alkaline solution with sodium perborate, removing the excess of the perborate by boiling, and after the addition of potassium iodide and dilute sulphuric acid, titrating with a standard sodium thiosulphate solution.—*Journal of Industrial and Engineering Chemistry*.

TOTAL SULPHATES IN LEATHER.

By Dr. L. E. LEVI and AUG. C. ORTHMANN.

In a former article we mentioned the fact that we had some 2000 odd leather analyses to make during the year. It is but natural that the most rapid and accurate methods be used in order to clear the way for other work.

We have found it highly essential to make the total sulphate determination in all leathers finished or unfinished, that have been tanned with a chrome sulphate compound. This determination in conjunction with the chromium content, will readily show the absence or presence, of free sulphuric acid in the leather.

Where a basic chrome sulphate liquor has been used for tanning and the basicity further reduced by subsequent addition of alkali carbonates or hydrates after the leather has been chrome tanned, to further set the chrome, and after thorough washing with water, free sulphuric cannot be present. The sulphuric acid found in such a case would be combined with chromium, aluminium, iron, calcium, sodium, and potassium, the last two are entirely removed on proper washing; thus by determining the chromium and the sulphates, and calculating the latter to H_2SO_4 , the proportion of one to the other will determine the chrome compound present, due allowance must be made for acid combined with aluminium, iron, and calcium.

Normal chromium sulphate, $Cr_2(SO_4)_3$, is a combination of 38.78 per cent Cr_2O_3 and 61.22 per cent SO_3 and if this proportion exceeds these figures it is a sure sign that free acid is present.

Realising the importance of this determination in that the basicity of leather could be easily controlled, the matter of selecting a rapid and accurate method for the same suggested itself. The bomb method, the nitric acid method, and the method of Balland and Maljean have been used in this laboratory up to the year 1914. These methods, however accurate, were found wanting regarding rapidity, neither of which could in any way be improved upon in this respect. The bomb method; an Emerson calorimeter bomb was used for this purpose, 1 gm. of leather was placed in a platinum shell which in turn was placed in the bomb, the lower part of the bomb was covered with sodium carbonate, then filled with oxygen at a pressure of about 25 atmospheres, and ignited by means of an electric current and iron wire; the released gases were led into a beaker containing N/10 alkali and the solid contents of the bomb were washed into this beaker with hot water, the whole acidified, boiled, and filtered, the filtrate boiled and treated with $BaCl_2$.

The nitric acid method of Wünsch and the sodium carbonate method of Balland and Maljean were carried

out as given in Procter's *Leather Industries Laboratory book*, second edition. pp. 370 and 371.

The method we finally adopted is as accurate as any of the above and at the same time more rapid than any of them. Chromic acid strongly acidified with hydrochloric acid is used to oxidise the organic matter, and any chromic acid not reduced in this way is reduced by means of alcohol, the remaining alcohol and resulting aldehyde are boiled off. The method is carried out as follows:—

The Reagent.—Take 50 grms. of chemically pure potassium bichromate and dissolve in 150 cc. of water; when dissolved add 50 cc. of chemically pure concentrated hydrochloric acid. Weigh out in 1 gm. of the fat free leather into a 250 cc. beaker and add 20 cc. of the reagent and bring to a gentle boil, then add 8 to 10 cc. of hydrochloric acid, let digest over a burner until all organic matter is destroyed. Then boil vigorously for two or three minutes, after which add about 50 cc. water and about 5 cc. of alcohol, boil until all chrome is reduced and alcohol and aldehyde is driven off, then add 50 cc. more water, bring to a boil and add barium chloride solution, let stand two or three hours, filter and wash precipitate and burn as usual.

In case a leather contains talc or allied substance filtration must take place before adding barium chloride.

	Weight BaSO ₄ grms.	Calculated to per cent H ₂ SO ₄ .
Bomb method	0.1032	4.3375
	0.1020	4.2870
Wünsch's nitric acid method	0.1034	4.3459
	0.1017	4.2744
Ballard and Maljean sodium carbonate method	0.1024	4.3039
	0.1032	4.3375
Chromic acid method	0.1012	4.2534
	0.1015	4.2660

A comparison of the different methods is given in the accompanying table. One gm. of finely divided fat free leather was used.—*Journal American Leather Chemists' Association.*

THE MANCHESTER AND DISTRICT DECIMAL ASSOCIATION.

It is generally admitted that the national welfare rests largely on our ability to maintain and increase the volume of our export trade. Other things being equal, trade naturally follows the line of least resistance, and we should accordingly so improve our avenues of commerce as to make them attractive to our customers abroad. As one important step in this direction we are advocating that our present unwieldy systems of coinage, weights, and measures should be abandoned in favour of a complete decimal system, such as our friends abroad would readily understand. The following general observations may serve to focus attention on the chief points which deserve consideration in connection with this reform.

Decimal Coinage.

The British Empire stands alone amongst the nations of the world—excluding only Siam and Persia—in her neglect to adopt a decimal system of coinage. It should also be borne in mind that the British Empire is not united in her isolation, as Canada and Ceylon, for instance, have already adopted decimal coinage, and both Australia and New Zealand are now contemplating a similar step. That it would be to our advantage to adopt a decimal system of coinage must be apparent from the fundamental fact that all our financial transactions, involving such everyday questions as rates of interest, dividends, discounts, commissions, &c., are based on a rate per cent, *i.e.*, per 100, and not per 20 or per 240. Our present system could be rearranged on a decimal basis without altering the existing

values of our gold and principal silver coins. For instance, we could adopt our present florin as the standard coin and divide it into 100 cents (instead of 96 farthings).

The sovereign and the half-sovereign would be retained, and the full set of coins would be as shown in the accompanying table.

Coins.	Value in present currency.	Cash entry (two columns only).	
		Florins.	Cents
Gold .. { Sovereign	Sovereign	10	00
	Half-sovereign	5	00
Silver .. { Florin	Florin	1	00
	Shilling		50
	Quarter		25
Nickel .. { 10 cents	2.4 pence		10
	5 cents		05
Bronze { 4 cents	0.96 pence		04
	2 cents		02
	1 cent		01

The 5 cent piece (say, 1½d.) would be available for such "pennyworths" as could not be supplied for the new 4 cent piece (say, 1d.). An example of the utility of this 5 cent piece is provided by the recent situation when newspapers were advanced from 1d. to 1½d. If the 5 cent coin had been available this price revision might have resulted in a 20 per cent instead of a 50 per cent advance. Hitherto the chief argument against the adoption of the above system has been that the values of our present bronze coins would be depreciated by 4 per cent, since there would be 100 cents instead of 96 farthings in the florin. But in these days, with our normal conception of values so violently disturbed by the war, it surely cannot be argued that a 4 per cent reduction in the purchasing power of the penny is a sufficiently powerful consideration to debar us from enjoying the benefits of decimal coinage. The present period of widely fluctuating values is obviously a most opportune time for revising our coinage system, and we are further helped by the circumstance that millions of our people are now gaining practical first-hand experience in the use of the decimal systems of coinage employed by our Allies. Alternative proposals, by which our present penny would be retained as the standard coin involving the introduction of new coins representing decimal multiples of the penny, have been advocated from time to time but hitherto with little success, probably because under any such scheme the £ sterling could not survive. It will be noted that under the Association's proposals the £ sterling is retained.

Metric Weights and Measures.

At present British manufacturers and merchants are compelled to work in the Imperial system of weights and measures for their home trade, and in the metric system for their trade with "Metric" markets abroad. The extra work and liability to error attendant on the necessary conversion of a metric enquiry into Imperial terms, and its subsequent re-conversion into the metric system, obviously hamper the British exporter in his efforts to develop his foreign trade. For many years our Consuls abroad have consistently advocated our adoption of the metric system. The ideal arrangement would be the establishment of one International system of weights and measures whereby the producers and consumers of the world could readily communicate without any necessity for conversions. Bearing in mind that, with the exception of the United States and Russia (in both of which countries a strong demand exists in favour of its adoption), practically all other civilised countries have already adopted the metric system, it should be clear that the British Empire can best accelerate the attainment of the above ideal by herself falling into line with these "Metric" countries. The scientific and practical advantages of the metric system have already been fully demonstrated, as is evident from its adoption as the universal language of quantity by the

scientists of the world and by its practical use in our newer industries, such as the manufacture of motor cars, aircraft, electrical apparatus, &c. Any attempt to impose our chaotic and cumbersome Imperial weights and measures upon the world would not only be foredoomed to failure but bring ridicule upon us. In some quarters there is a tendency to recommend the adoption of a middle course, viz., to decimalise the present British units of weights and measures. The advocates of such an intermediate step have progressed so far as to acknowledge the defects of our present system, and to appreciate the advantages of a decimal basis, but they cannot yet bring themselves to the point of definitely abandoning the British units notwithstanding their inherent defects. Although the abandonment of the lb. weight and the yard measure in favour of the kilogram and the metre may sound alarming to some, there can be no doubt that the resultant benefits, accruing to the whole community, would speedily far outweigh any temporary difficulties and inconveniences encountered during the period of transition. In practice it would be found during this period of transition that whereas new standards would naturally be based on the metric system, all existing standards could remain in use for manufacturing purposes until, in the normal course of development, they became obsolete.

Summary.

From the foregoing observations it will be apparent that we should derive considerable assistance from the universal adoption of a decimal system of coinage and the metric system of weights and measures. The extreme simplicity of these rational methods is demonstrated by the fact that, according to expert opinion, their adoption in lieu of our present systems would result in a saving of more than a year in the school life of the average child. This valuable time could obviously be put to good service by, for instance, acquiring some knowledge of science and modern languages. We must expect that Germany's competition for the trade of the world will be more strenuous than ever, and it accordingly behoves us to put our house in order now, instead of complacently postponing our consideration of these problems until after the war. The course of recent legislation proves that the general public is at present more receptive of new ideas than at any previous time in history, an instance in point being the ready adoption of the Daylight Saving Bill.

Our Objects.—Our objects, in common with similar Associations in various parts of the country, may be defined briefly as follows:—To urge upon the Government—(a) The early adoption of a decimal system of British coinage. (b) The compulsory use, after a suitable transition period, of the metric system of weights and measures in the United Kingdom, and, if possible, throughout the British Empire.

Terms of Membership.—There are two classes of subscribers, namely:—Members—Subscription, one guinea per annum, being firms, companies, and individuals desirous of giving substantial support. Associate members—Subscription, five shillings per annum, comprising others who, by paying a nominal subscription, can assist the Association in its advocacy of the reforms herein described.

No reform can be accomplished unless it has widespread support, and the Council accordingly urge all those who approve of their proposals to support the Association by joining forthwith.

All communications should be addressed to the Acting Secretary, Mr. FRED HILTON, 55, Market Street, Manchester.

Aluminium Hydroxide Test.—In the bulk of oils powdered aluminium hydrate gelatinises, functioning its subdivision in particles as a test for water and oils.—J. C. T.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, January 18, 1917.

Dr. ALEXANDER SCOTT, M.A., F.R.S., President,
in the Chair.

THE PRESIDENT referred to the loss sustained by the Society, through death, of James McConnan and Raymond William Nichols (killed in action); Robert Glegg, Allan Wisleton Hall, Norman Harry John Miller, John Northing, Thomas Wilton, and George James Woods.

Messrs. Charles A. Schunck, A. W. H. Upton, and Leslie N. Brown were formally admitted Fellows of the Chemical Society.

Certificates were read for the first time in favour of Messrs. Samuel Comber Atkinson, B.Sc., 29, Gatling Road, Plumstead, S.E.; Frank Bayley, M.Sc. Tech., The Bungalow, Pound Road, Warley, Birmingham; Percival Joseph Channon, Romney, Haywards Heath, Sussex; Charles Edwin Corfield, 17, Bloomsbury Square, W.C.; Francis William Buckland Cunningham, B.Sc., Hytesbury, West End Lane, Hampstead, N.W.; Biman Bihari Dey, D.Sc., Presidency College, Calcutta; Roland Hall, 614, Holderness Road, Hull; John Carol Johnson, 9, Well Road, Hampstead, N.W.; Alfred Godfrey Gordon Leonard, B.Sc., Ph.D., 1, Clareville Road, Rathgar, Dublin; Ernest William Moss, 12, Windermere Avenue, Church End, Finchley, N.; Alfred Nuttall, Corner 16th Avenue and Robinson Street, Regina, Canada; Herbert Eustace Nickels, 293, Wanstead Park Road, Ilford; Walter Parker, 8, Clarendon Grove, Haulgh, Bolton; William Payman, M.Sc. Tech., 7, Darlington Street, Cheetham, Manchester; Frank Henry Pugh, B.A., 2, Cotnam Street, Walworth, S.E.; Gunendranath Raye, Gauhati, Assam, India; Felix Johan Tromp, B.A., Messrs. Levinstein, Ltd., Blackley, Manchester; Allan Whitehead, 5, Lawrence Street, Waterfoot, Manchester.

A Certificate for election has been authorised by the Council for presentation to ballot under By-law I. (3) in favour of Kumār Nāth Bāgchi, Government Laboratory, Gulzarbagh P.O., Patna, India.

Colonel C. T. Heycock, M.A., F.R.S., delivered a lecture entitled "Alloys of Copper and Tin, Aluminium and Gold."

A vote of thanks to the Lecturer was carried with acclamation.

SOCIETY OF GLASS TECHNOLOGY.

Ordinary Meeting, January 18, 1917.

W. F. J. WOOD, B.Sc., President, in the Chair.

THE Rules and Constitution were passed, and it may be of value to intending members to quote the following:—

- The Society shall consist of—
 - Collective Members*—i.e., firms who are engaged in the manufacture, distribution, or use of glass.
 - Ordinary Members*—i.e., persons (not being either representatives of collective members or student members) who are interested in glass technology.
 - Student Members*—i.e., registered students who are attending a course or courses of technical instruction in the United Kingdom.
- The Annual Subscription shall be as follows:—(a) Collective Members, £3 3s.; (b) Ordinary Members, £1 1s.; (c) Student Members, 2s. 6d.
- Application for Membership should be sent at once to the Secretary, Society of Glass Technology, The University Sheffield.

The election of Mr. E. B. Peacock as Member of Council and Messrs. G. Wilson Clarke and F. Lax as Auditors completed the formal business of the meeting.

The following papers were read:—

"British Glass Sands: their Location and Characteristics." By Dr. F. G. H. BOSWELL.

The author began by stating that the analysis of British sands had proved their value. The analysis of sand can be carried out in three ways—(1) Chemical, (2) Mechanical, (3) Mineral.

Chemical analysis proves the value of a sand by determining its silica content, which must be high, and its iron content, which must be low. In the past, sands with higher iron oxide content than 0.02 per cent were regarded as useless for the best types of glass, but recent work has shown a higher iron content to be permissible, and so British sands can be used for good glass.

Mechanical analysis determines the grading of the sand, the best for glass being that with the largest percentage of grains of diameter 0.25 to 0.5 mm.

Mineral analysis is important in the laboratory for controlling consignments of sands, and also gives an indication of impurities to be expected.

Slides were shown to illustrate the microscopic appearance, chemical composition, and grading of sands.

The relative value of crushed rock was discussed, and it was shown that, after crushing, screening and washing were necessary to remove the larger grains and the fine material. By means of a geological map the position of English sand deposits and their situation relative to the centres of the glass industry was ably illustrated. The paper closed with a consideration of the transport question, and the need for development of the canal system together with a cheapening of railway rates.

"British Glass Sands: the Substitution of Foreign Sands by British Sands for High Grade Glass Making." By C. J. PEDDLE.

In the first place the author summarised the essentials of a good glass sand from the manufacturer's point of view, and showed that it must contain a high percentage of silica and a low percentage of impurity, particularly iron oxide. It must be evenly graded, and the grains should be angular. In addition, a sand should always be true to sample, and consignments should not vary, nor should there be any treatment necessary at the hands of the manufacturer. All these essentials are fulfilled by Fontainebleau sand, but not all by any British sand as at present supplied. That some British sands compare favourably with Fontainebleau, both as regards purity and grading, has been established by the author, whose results in general are in agreement with those of Dr. Boswell. In addition, a long series of melts also support this view, and on this account the statements of Dr. Rosenhain as to the non-availability of British sands for good glass are to be criticised. Splendid results are obtainable with British sands which have been properly treated, and numerous specimens of glasses made from British sands were exhibited side by side with the sands. Several of these glasses could not be distinguished from similar melts made with Fontainebleau sand, being just as brilliant and colourless.

The question of treatment was then discussed, and the necessity for washing and grading was thoroughly demonstrated by a series of microphotographs, by chemical analysis, and by actual melts. The need of proper scientific treatment of British sands and the necessity of putting them into the manufacturer's hands ready for immediate use was emphasised, and it was pointed out that unless this treatment was forthcoming, together with attention to mode of delivery, British sands could not hope to compete favourably with Fontainebleau.

DISCUSSION.

Prof. W. G. FEARNSIDES (Sheffield) advocated the co-operation of the glass manufacturer and the sand merchant,

as the latter was not in a position to provide washing plant.

Mr. F. G. FOSTER (Birmingham) stated that the greatest difficulty before the sand merchant was to obtain an efficient washer at a low price. In addition, the amount of first-class sand required would not in many cases repay the original outlay, and this, coupled with prohibitive railway rates, tended to stifle enterprise.

Mr. G. DOWSE (London) pointed out that the demand for good sand was daily increasing, and efforts were being made to place a better British sand on the market than had hitherto been obtainable.

Mr. J. McCORMICK (Scarborough) emphasised the fact that the steel manufacturer will give 15s. per ton for untreated sand, whereas the glass manufacturer expects to get it washed, graded, and dry at 3s. The difficulty is not in designing a sand washer, but in making it pay.

Dr. BOSWELL said that too much must not be expected of the sand merchant, as the margin of profit was very small. A great advance would be to get railway freights lowered and water traffic taken up. Great improvements in British sands were observable of late, and the future was hopeful.

Mr. PEDDLE was of the opinion that the crux of the whole matter lay in a proper understanding of the glass manufacturer's wants. He felt sure that the British sand merchant could compete with the foreign sand merchant both as regards quality and price if the question were only tackled properly.

The next meeting of the Society will be held in The University, Sheffield, on Thursday, Feb. 15, at 4.30 p.m. Papers will be given on "The Annealing of Glass."

BRITISH ASSOCIATION OF TRADE AND TECHNICAL JOURNALS, LTD.

THE incorporation of the Association as a Company limited by guarantee has now been completed, and it is hoped that new members will now be obtained on this ground. The address of the Association is now changed to Kingsway House, Kingsway, W.C.

The following is a summary of proceedings at a private meeting convened at Holborn Restaurant on December 8, 1916, by the British Association of Trade and Technical Journals.

Mr. W. A. STANDRING, Chairman of the B.A.T.T.J., explained that the meeting was called in consequence of appeals having been made to the business Press to declare a policy in regard to the advertising of enemy goods after the war. It was hoped that the meeting would lead to co-operation of associations for giving practical effect to some settled policy.

Mr. PERCIVAL MARSHALL (B.A.T.T.J. Council) moved: "That in the opinion of this meeting it is desirable that British manufacturers and producers and British trade and technical journals should co-operate as closely as possible in the promotion of British trade interests, and that such co-operation can best be effected through the mutual recognition and utilisation of the respective associations. Mr. Marshall stated that the British Association of Trade and Technical Journals had now attained an influential position, and could do a great deal for the joint interests of all branches of British commerce.

Sir CHARLES BEDFORD (Association of British Chemical Manufacturers), in seconding the resolution, urged the need for co-operation and co-ordination and the proper allocation amongst different agencies of the industrial problems arising out of the war, particularly in connection with increased production and the finding of markets. In such matters the trade journals could have an enormous influence in educating public opinion.

The resolution was carried unanimously after a short discussion.

Mr. T. C. ELDER (Hon. Secretary, B.A.T.T.J.), who

moved: "That associations of manufacturers and producers should confer together with the British Association of Trade and Technical Journals in order to formulate a consistent policy in regard to such matters as the advertising of enemy and neutral goods after the war and the attitude that should be adopted towards importers and factors of such goods," said that it was necessary for each association to consider after-war relations with our present enemies. The publicity power of the trade journals was at their service, but the Press would reflect the policy adopted by these associations and by the Government.

Mr. HORACE WYATT (Association of British Motor and Aircraft Manufacturers), in seconding the resolution, claimed that the Press should not reflect the views of the country or of sections, but should give a lead. He would like a policy to be formulated that all journals would adopt provided the manufacturers gave corresponding guarantees.

Sir GEORGE MACKILL, Bart. (British Empire Producers' Organisation) approved of further conference, and suggested that it might be expedient to have a higher scale of charges for advertising neutral and enemy goods somewhat proportionate to the proposals of the Paris Conference.

Mr. OTTO THOMAS (*Motor Traction*) appealed for a strong declaration of policy, regardless of minor practical difficulties which would have to be considered and overcome later.

Mr. D. N. DUNLOP (British Electrical and Allied Manufacturers' Association) said that it would be fair to expect that if the rejection of enemy advertising meant a serious sacrifice of revenue on the part of the members of the Association of Trade and Technical Journals, the Association of British Manufacturers should in some way make that good. He saw great possibilities in further conference.

Mr. HERBERT WILLIAMS (Machine Tool Association) said that whatever plan might be adopted they would have to meet certain practical difficulties such as the purchase by enemy interests of weaker journals which might be converted to the service of alien firms.

Mr. FRANCIS (Paper Makers' Association) suggested that some statement should be prepared outlining a suitable policy for the consideration of all associations concerned.

Mr. VICKERS (*Indian and Eastern Engineer*), Mr. DODD (*Canadian Machinery*), and others followed.

The resolution was carried unanimously.

At a meeting of the Council of the British Association of Trade and Technical Journals, on December 18, it was decided to invite the following gentlemen representing associations of manufacturers:—Sir George Mackill, Bart., Sir Chas. Bedford, Messrs. D. N. Dunlop, H. Williams, H. Wyatt, and R. T. Nugent to meet a sub-committee to consider what practical steps can be taken for the more effectively organised co-ordination of British production and publicity.

NOTICES OF BOOKS.

Practical Experiments in Heat and Light. By W. ST. B. GRIFFITHS, B.A., B.Sc., and P. T. PETRIE, M.Sc., Assoc.M.Inst.C.E. London: Rivingtons. 1916. Price—One vol., 3s. 6d. net; or, in two Parts, "Heat," 2s. net; "Light," 1s. 6d. net. Pp. iv. + 123; viii. + 112.

THIS book appears to be a thoroughly useful guide to experimental work in heat and light. It contains descriptions of such experiments as can be performed by young students themselves with the apparatus usually to be found in the average well-equipped physical laboratory, no lecture table experiments being included, nor any

which are best left to skilled hands. The directions are clear and full, and the average student would probably have no difficulty whatever in carrying out the experiments and calculating his results without any help from a teacher. The volume includes 59 experiments in heat and 68 in light, and the whole ordinary course of elementary work is covered. The experiments are, as a rule, of the usual type, and display no particular novelty, but they represent a very useful collection, designed to give the student a thorough working acquaintance with the elementary principles of heat and light.

Chemistry for Rural Schools. By ERNEST JONES, M.Sc., and J. JONES GRIFFITH, B.Sc. London, Glasgow, and Bombay: Blackie and Son, Ltd. 1916. Pp. 184. Price 2s. 6d. net.

THIS book is intended to be used as a theoretical and practical introduction to agricultural chemistry for students in technical schools and agricultural colleges, and at the same time the authors believe that it may be found useful for general students who are beginning chemistry, but do not mean to specialise in scientific agriculture. The early part of the book describes the usual operations of elementary practical chemistry—measuring, weighing, and the study of chemical and physical changes—and then the chemistry of the atmosphere is taken up, followed by experiments on oxygen, acids, hydrogen, and salts. Some account is given of the laws of chemistry and of the atomic theory. In the later part of the book, which deals with the common elements and their compounds, the experiments are mostly chosen with a view to the application of the student's knowledge to the problems of agriculture, and such subjects as the fixation of atmospheric nitrogen, the assimilation of carbon dioxide by plants, animal nutrition, the constituents of the soil are discussed in outline with illustrative experiments. Most boys and girls would find the course of work described interesting, and the spread of the kind of knowledge it imparts is of vital importance at the present moment. The book appears a satisfactory pioneer of the new movement of which signs are to be discerned in recent discussions regarding the curricula of our schools; the authors have chosen their material sensibly, and have not attempted too much, and the wide adoption of the book in rural schools would be a decided step forward in the right direction.

The International Movement of Fertilisers and Chemical Products Useful to Agriculture. Rome: The International Institute of Agriculture. 1916. Pp. 76. Price 1.50 fr.

THIS reprint from the "International Crop Report and Agricultural Statistics" appears very opportunely at the present moment. It gives full and detailed information relating to the production, trade, consumption, and prices of all important chemical fertilisers and also sulphur and copper sulphate. Most of the trade statistics are official, and every effort has been made to make the data relating to the consumption in various countries as full and accurate as possible. A useful bibliography of the world's literature on the subject of artificial fertilisers is included.

Literary Intelligence.—Mr. Lloyd George has accepted the dedication to Mr. Arthur Marshall's celebrated book on Explosives. The second edition, much enlarged, will appear in two volumes—the first of which will be ready immediately, and will contain a handsome portrait of the Prime Minister. Mr. Marshall's book is the only recent treatise in the English language on a subject which is of national value at the present time. Messrs. J. and A. Churchill are the publishers.

OBITUARY.

MR. ANDREA ANGEL.

THE death of Mr. Andrea Angel, M.A., F.C.S., B.Sc. (Oxon.), who heroically sacrificed himself in the explosion at the munitions factory near London, on Friday, January 19th, is a great loss to chemical science and will be very deeply lamented by his colleagues and his wide circle of acquaintances and friends. When the fire broke out he, perhaps more fully than anyone else, realised the terrible danger of explosion, but with the utmost self-forgetfulness and devotion to duty he did his best to warn others and to fight the conflagration, and thus went to his death without flinching.

Mr. Angel was born at Bradford, Yorkshire, in 1877. He received his education at Exeter Grammar School and at Christ Church, Oxford, taking a first-class in Chemistry in 1899. He took his M.A. degree in 1903 and B.Sc. in 1906. He was appointed Lecturer in Natural Science at Brasenose College, Oxford, and tutor to the non-collegiate students, and his success as a teacher was remarkable, many of his students having reason to be thankful that they had the advantage of coming under his stimulating influence. A short time ago he became chief chemist at the factory at which the explosion occurred, and there he exhibited the same thoroughness and assiduity which had marked his work as a teacher.

MISCELLANEOUS.

University College.—A special Introductory Medical Course in Physics, Chemistry, and Biology for students desirous of beginning their medical studies will be held at University College, beginning on March 1. Intending students should communicate forthwith with the Secretary, University College, London, Gower Street, W.C.

Institute of Chemistry.—Pass List January (1917) Examinations.—The results of the examinations of the Institute of Chemistry recently held in London have now been published. Four candidates passed the Final (A.I.C.) Examination, viz.:—In the Branch of Organic Chemistry—J. W. Ingham, B.Sc. (Lond.), and E. W. J. Mardles, B.Sc. (Lond.). In the Branch of the Chemistry (and Microscopy) of Food and Drugs, Fertilisers and Feeding Stuffs, Soils, and Water—Alan Haythornthwaite, B.Sc., A.R.C.S. (Lond.), and Ernest Paul, B.Sc. (Lond.).

The Great War.—Government Requisitions of Wine for French Soldiers.—Messrs. James L. Denman and Co., Ltd., 20, Piccadilly, London, send us the following important information:—It is apparently not generally known that throughout the present war the French Government has requisitioned millions of bottles of Claret or Red Wine for consumption by officers and men of every rank in the Armies of the Republic. When this fact was first published by us, inquiries as to its accuracy came to hand from temperance organisations, as well as from private individuals who were surprised to learn that the practice had been adopted by our Continental neighbours upon the highest medical advice, with a view to preserve the health of the troops in the very trying conditions to which they were exposed by trench warfare and other features peculiar to the campaign. We therefore communicated with the French War Ministry, and are now able to give precise particulars in confirmation of our statement. The official returns furnished show that in 1915 the French Government requisitioned and purchased 4,685,000 hectolitres, or more than six hundred and eighteen million large bottles of Claret or Red Wine, for the use of its armies. Each officer and man daily receives half a litre of wine, and the actual number of bottles requisitioned in the year mentioned was 927,630,000 half litres. During the following twelve months of 1916, when the forces engaged in the

different theatres of operation had been largely increased, the total quantity of wine requisitioned by the Government of the Republic is estimated at 6,000,000 hectolitres, representing one thousand one hundred and eighty-eight million half litres=792,000,000 large bottles. In the opinion of the Medical Staffs of the French Armies, the daily consumption of wine has contributed in a very material degree to the magnificent health which all ranks have enjoyed since the beginning of the war. This is particularly apparent on the Eastern front, where we understand that the example has been followed with equal advantage in the case of the British troops. The experience also confirms that obtained upon our own Chateau Livran Estate, where, in the hospital established under the French Red Cross Society, several hundreds of wounded and sick soldiers have had a generous allowance of wine which, in the opinion of the medical attendants, has assisted their rapid and complete recovery.

Burmese Myrabolans as a Tanning Material.—According to the *Indian Trade Journal* of September 15, a report on the Burmese myrabolans or "pangia" fruits as a tanning material, prepared by the chemical adviser to the Forest Research Institute, states that the Burmese myrabolans are different from the Indian Chebulic myrabolans in points of tannin and non-tannin contents and colour. In the air-dried Burmese material the tannin varies from 16 to 32 per cent; the general average may thus be taken to be 20 to 25 per cent, which is about half the tannin content of the Indian myrabolans. The non-tannin ranges from 25 to 34 per cent, and the general average may be taken to be 27—30 per cent, which is three times that of the Indian myrabolans. The colour is high. The maximum red and yellow recorded for the Indian myrabolans is 2.5 red and 7.4 yellow, while the Burmese myrabolans in general have 4.9 red and 18.35 yellow. The excess of non-tannin is a disadvantage, and all tanning materials having non-tannins in excess must be classed as somewhat inferior, though in practice they give fairly good results. To form some opinion as to the actual tanning properties of the Burmese myrabolans experiments were undertaken, which disclosed that leather made with this material alone is spongy and tough like the leather produced by Indian myrabolans, that the Burmese fruits can be used in the preparation of butts for making army boots and shoes, and also for making black uppers of inferior quality, and that they will be useful in conjunction with babul bark for making sole leather.—*Chemical Engineer and Manufacturer*, xxiv., No. 5.

MEETINGS FOR THE WEEK.

- MONDAY, 5th.—Royal Society of Arts, 4.30. (Cantor Lecture). Town Planning and Civic Architecture," by Prof. Beresford Pite.
— Roy Institution, 5. (General Meeting).
TUESDAY, 6th.—Royal Institution, 3. "The Old Brain and the New Brain, and their Meaning," by Prof. C. S. Sherrington.
— Röntgen Society, 8.15. "Some Properties and Applications of Selenium," by E. E. Fournier D'Albe, D.Sc.
WEDNESDAY, 7th.—Royal Society of Arts, 4.30. "The Future of British Spas," by R. Fortescue Fox, M.D.
— Society of Public Analysts, 8. (Annual General Meeting). "Quantitative Estimation of Mercury in Organic Compounds," by J. E. Marsh and O. G. Lye. "Shrewsbury and Knapp Process for the Detection of Coconut Oil," by G. D. Eldon. "Detection of Rose Petals in Blue Pill," by W. Partridge.
THURSDAY, 8th.—Royal Institution, 3. "The Mechanism of Chemical Change," by Prof. F. G. Donnan.
— Royal Society. "Dynamics of Revolving Fluid," by Lord Rayleigh. "Deflection of the Vertical by Tidal Loading of the Earth's Surface," by H. Lamb. "Spontaneous Generation of Heat in Recently Hardened Steel," by C. F. Brush and Sir R. Hadfield.
FRIDAY, 9th.—Royal Institution, 5.30. "Experimental Phonetics and its Utility to the Linguist," by Daniel Jones, M.A.
SATURDAY, 10th.—Royal Institution, 3. "Colour from Diaphony to Debussy," by H. Walford Davies, Mus. Doc.

THE CHEMICAL NEWS

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ON THE ESTIMATION OF MANGANESE IN HIGH SPEED STEELS.

By C. T. NESBITT, A.R.S.M.

OWING to the difficulty of obtaining some reagents—more especially bromine—on the outbreak of war, the question of a good method for estimating Mn in high-speed steels, without the use of bromine, became of importance. For the last two years various methods and modifications of methods have been extensively tested, and their advantages and disadvantages noted. These methods and modifications will be explained and discussed in the present paper. They apply to all high-speed steels proper; *i.e.*, those containing high percentages of tungsten and chrome, tungsten-chrome-vanadium, or tungsten-chrome-vanadium-molybdenum. They will also apply to the ordinary alloy steels of commerce.

There are three main classifications of the various methods:—

- (a) The gravimetric or basic acetate method.
- (b) The ZnO or CdCO₃ separation method.
- (c) The more or less direct bismuthate methods.

(a) *The Gravimetric Method.*—It is unnecessary to go into the standard gravimetric or basic acetate method in any great detail, as it is well explained in many textbooks. Shortly, the process is as follows:—

Four grms. of steel drillings are dissolved in HCl. When in solution oxidise with 5 cc. concentrated HNO₃, boil down to low bulk, take up with dilute HCl (30 cc. HCl and 70 cc. H₂O), boil, filter off the tungstic oxide, and wash well with water. Make up filtrate to about 900 cc., and raise to boiling. Neutralise first with strong AmHO, and when near neutralisation finish with dilute AmHO or Am₂CO₃ till any further addition would bring down a precipitate. Add 50 cc. Am acetate solution, and boil. Make up to 1000 cc., and take the temperature. Filter of 500 cc. through a dry filter, adjusting the temperature of the filtrate. Boil down to low bulk—say, 100 cc.—filter if necessary, cool, oxidise with 2 cc. bromine for fifteen minutes. Add excess AmHO, and heat till MnO₂ precipitate is coherent. Filter, wash, burn off at a high temperature, and weigh the residue of Mn₂O₄. Calculate to Mn.

This standard method works well with every class of steel—high-speed alloy or plain carbon. It is not an easy estimation owing to the neutralisation point requiring a considerable amount of practice. When that is acquired, however, the rest of the procedure is simple and accurate.

When bromine was almost unprocureable the following modifications were tried:—

(i) After the basic acetate separation the 500 cc. of filtrate was boiled down with 10 cc. concentrated H₂SO₄ to fuming. This was to decompose and drive off all ammonia salts, and especially all chlorides. The residue was diluted with 60 cc. 1:2 HNO₃, and the manganese estimated by oxidation with bismuthate and titration with FeSO₄ and KMnO₄—see (c) bismuthate methods. This modification was tested daily for several weeks against the standard gravimetric method and found to give results on the low side. The average is between 0.03 and 0.06 per cent low on a 0.35 per cent manganese steel. The method was discarded owing to the above and because it was found to be impossible to get out results in an ordinary working day, unless the gas (hot plate) was exceptionally good and hot—a consummation devoutly to be wished for, but not obtained under war conditions.

The other modifications tested were in the direction of replacing bromine with some other oxidising agent. The following were tried:—

- (2) Ammonium persulphate.
- (3) KClO₃ and HCl; *i.e.*, chlorine.
- (4) and (5) H₂O₂ and Na₂O₂.

(2) *Ammonium Persulphate.*—If the 500 cc. filtrate from the basic acetate separation is boiled down to about 200 cc. filtered if necessary, and then boiled again with 1 gm. ammonium persulphate, the manganese can be satisfactorily precipitated as the hydrated MnO₂ with AmHO, if the persulphate is absolutely pure. When first tried the results obtained were all about 0.1 per cent too high. This was proved to be due to impurities in the persulphate. Numerous tests gave approximately 3 mgrms. impurities per 1 gm. of persulphate. This salt was the ordinary reagent as supplied by dealers. At present no ammonium persulphate sufficiently pure to be used satisfactorily has been obtained; otherwise this method of oxidation would be eminently cheap and good. The method has been proved practically by estimating the impurities (SiO₂, Fe₂O₃, Al₂O₃, &c.) in the Mn₂O₄ residue and deducting.

(3) *Chlorine.*—The addition of KClO₃ and HCl as a means of producing chlorine for oxidising the Mn is not altogether satisfactory. It appears that the ammonia salts (chloride, acetate, &c.) very often have the property of dissolving up the MnO₂ first precipitated by AmHO. In fact, this means of oxidation is only applicable when the solution is moderately pure and does not contain a large amount of ammonia salts—a condition rarely fulfilled in the basic acetate filtrate. It can be used fairly successfully by evaporating the filtrate to dryness with aqua regia to drive off ammonia salts, taking up with HCl, and then oxidising by the addition of 3 grms. KClO₃ heated with 20 cc. of 50 per cent HCl till Cl₂ begins to come off. On heating, the Mn is oxidised and can be precipitated in the usual way by excess AmHO. It is obvious that this method is either unsafe or much too long.

(4) and (5), H₂O₂ and Na₂O₂.—These oxidising agents appear to act very much in the same way as chlorine. It is necessary to have a moderately pure solution of Mn before oxidising, otherwise the precipitated MnO₂ goes into solution again on heating. A large number of experiments on basic acetate filtrates failed to find satisfactory conditions for oxidation of Mn by these reagents.

Summing up, the alternatives to the bromine method of oxidation in basic acetate filtrates, with the exception of ammonium persulphate, are too unreliable for use. Ammonium persulphate appears to be satisfactory, but must be absolutely pure or the Mn₂O₄ is contaminated.

(b) *ZnO or CdCO₃ Methods.*—These methods are more generally used in America. The procedure is as follows:—Weigh out 4 or 5 grms. of steel drillings and dissolve in 60 cc. 25 per cent H₂SO₄. Oxidise with 5 cc. concentrated HNO₃. Boil down to low bulk and take up with 60 cc. 1:2 HNO₃. Filter off tungstic oxide and wash. Make up to about 400 cc., and add an emulsion of ZnO or CdCO₃ till all the iron and chromium are thrown down. Make sure there is a slight excess of Zn or CdCO₃. Make up to 500 cc. and filter off 250 cc. through a dry filter, making the usual temperature correction if necessary. Boil the filtrate down to one-half its volume. Add 10 cc. concentrated HNO₃, cool, add sodium bismuthate, filter through asbestos, wash with dilute HNO₃, and titrate with FeSO₄ and KMnO₄.

It was found that better results were obtained by adding the emulsion in the cold, though every published account of the method advocates a boiling temperature. This is possibly due to the large amount of chromium present, as the method works equally well hot or cold on plain carbon steels. There seems to be little difference in the precipitation properties of ZnO or CdCO₃ emulsion; ZnO is, of course, always used owing to its greater cheapness.

This method tends to give slightly lower results than the

standard gravimetric. In a series of forty duplicate analyses, sixteen gave results agreeing with the gravimetric, the remaining twenty-four giving results varying from 0.02 per cent to 0.06 per cent low on a 0.4 per cent Mn. These low results might, of course, be due partially to experimental error both in the gravimetric and ZnO methods, but all results varying over 0.4 per cent were again checked, and there were no results by the ZnO method appreciably higher than the gravimetric. Where results are not wanted nearer than 0.05 per cent, and these always on the low side, the method is a satisfactory one, and fairly easy and rapid to work.

A somewhat similar method was published by Mr. J. A. Cashmore in the *CHEMICAL NEWS*, vol. cxiv., No. 2973, but he did not state whether it was applicable to high-speed steels. The only obvious modification necessary would be replacing the $\text{K}_2\text{Cr}_2\text{O}_7$ used for oxidation purposes by HNO_3 , boiling down and filtering off the tungstic oxide precipitated, before proceeding with the ZnO precipitation. Mr. Cashmore, instead of finishing by the bismuthate method, oxidises with ammonium persulphate, precipitates his Mn with AmHO , and finally weighs as Mn_2O_4 . In this connection—see remarks upon ammonium persulphate previously explained.

Attempts to oxidise with bromine and chlorine and precipitate the Mn with AmHO , in the filtrate from the ZnO separation were not successful. High results were obtained in every case. It seems to be impossible to wash out all zinc salts from the manganese dioxide precipitate.

(c) *Bismuthate Methods*.—Among the many modifications of the bismuthate method, supposed to be adapted for high-speed steels, there appears to be only one which is at all satisfactory, and even in this modification the conditions have to be very carefully observed, any slight deviation usually resulting in extraordinarily high results.

Much work on this method has evolved the following as being probably the best method of procedure:—

Weigh up 1.1 grm. steel drillings and dissolve in 12 cc. concentrated HCl. Add 5 cc. concentrated HNO_3 and take down to syrupy consistency but not quite dry. Add exactly 7 cc. concentrated H_2SO_4 , and wash once round the sides of the beaker with water. On shaking, the estimation goes to a thick cream on the bottom. Leave on edge of hot-plate for twenty minutes, the beaker may then be placed in the centre of the hot-plate and fumed very strongly for fifteen minutes. Cool, take up with 30 cc. 1.2 HNO_3 and 20 cc. water. Boil and filter off tungstic oxide. This oxide is somewhat slimy and difficult to filter, but if filtered on to pulp and the top surface broken up with a wash-bottle jet it can be washed four times or more in about five minutes. To the filtrate add 15 cc. concentrated HNO_3 , to bring the strength of the containing acid to roughly 1.2 sp. gr. Boil and add a pinch of bismuthate, clear with 10 cc. H_2SO_4 . Boil off SO_2 and cool the estimation quickly under the tap. Now oxidise with about 0.2 grm. Na bismuthate, shaking for two or three minutes. Filter through asbestos, using a filter-pump to ensure rapidity. Wash with 3 per cent HNO_3 and titrate with N/10 FeSO_4 and KMnO_4 . The ferrous sulphate is added till all permanganate colour is discharged, and then the pink colour is brought back again by means of N/10 KMnO_4 . The end-point must be taken to permanent pink, i.e., a pink that is permanent for at least five minutes. There is a fleeting pink tinge obtained some few points of a cc. before the real end-point. This must not be confused with the real end-point or results will be high. Under the above conditions—

1 cc. N/10 FeSO_4 equals 0.1 per cent Mn.

This method is quite satisfactory if great care is taken concerning the following points: Tungsten should be thoroughly oxidised and removed; all chromium must be properly reduced—this is done in the first place by strong fuming with H_2SO_4 , and in the later stages by addition of H_2SO_3 .

Again, all chlorides must be driven off, which is a function of the fuming with H_2SO_4 ; and, lastly, titration must be taken to the proper end-point. Of course, if preferred, the titrating solutions can be standardised in the actual assay solutions, so that the end point can be varied to suit the operator to a certain extent. However, if N/10 solutions are used, or results calculated to N/10 strength by factor and the end-point is taken to a permanent pink, the results are in absolute agreement with the gravimetric method.

At first sight it appears to be somewhat absurd to dissolve up in HCl and convert to a sulphate solution when the steels will dissolve easily in dilute H_2SO_4 . On testing, however, it will be found that taking up in HCl and oxidising and then converting with H_2SO_4 is far quicker; in fact, can be done in less than half the time it takes to get an original H_2SO_4 solution oxidised with HNO_3 down to fuming. The H_2SO_4 solutions have a much greater tendency to spit, and must be evaporated exceedingly carefully and slowly. The aqua regia solution with H_2SO_4 added at the right time can be evaporated to fumes with little trouble.

One other little point in the manipulation of this method which should be watched is in boiling off SO_2 ; the estimation should not be boiled for more than a minute after all SO_2 is off, otherwise there is danger of oxidising some chromium, with consequently high results.

This last bismuthate method is by far the quickest of all the methods tested and reviewed. Six estimations can be done easily in under three hours, and leave a large portion of the time free for other work. Practically all the other methods take more than twice this time.

OBSERVATIONS UPON THE ATMOSPHERIC CORROSION OF COMMERCIAL SHEET IRON.*

By E. A. RICHARDSON and L. T. RICHARDSON.

THE corrosion of iron and steel is a question that is becoming of increasingly great importance. The problem of finding the true nature of and the ultimate causes that underlie the rusting of iron is as yet unsolved. Much work has been done in the past, is being done at present, and before the problem is solved much more will undoubtedly be done in the future.

The paper will not burden itself with a lengthy review of previous work that has been done upon the subject, but will confine itself to a brief summary of such work.

As regards the relative merits of wrought iron and steel much work has been done, but observations on the two materials seem to be in poor agreement.

Of recent years the question of the rust-resisting properties of copper-bearing steels has arisen and remains as yet unsettled, the chief contenders being the makers of copper-bearing steel and those of pure iron. As far as numerical data are concerned, the advocates of copper-bearing steel seem to be in the lead; in fact, it seems to the writers that one weakness in the argument of the iron advocates is that they give little numerical data to support their claims. To many their arguments would carry much more weight if such data were included.

Briefly, up to about 1910, a considerable amount of work had been done upon the subject of copper in steel, but this work was mainly in the form of fragmentary observations on steels that contained small quantities of copper either accidentally or intentionally added, and a few actual tests upon copper bearing material. Previous to this time there appeared to be no acute controversy as to the effect of copper in steel upon corrosion, although

* Paper presented at the 30th General Meeting of the American Electrochemical Society, New York City, September, 1916. From the *Chemical Engineer and Manufacturer*, xxiv., No. 4.

judging from the literature it did exist at this time to a rather mild extent as to the effect of this metal upon the physical properties of steel. The general impression one would gain from reading these articles, is that copper in steel is a benefit as regards resistance to corrosion.

Shortly after 1910 copper-bearing steel was put upon the market as a corrosion-resisting material. The controversy then became acute, the chief objectors being the advocates of pure iron. The result has been that a considerable amount of work has been done and published without settling the question. Most of this work seems to have been done by those interested in copper-bearing steel in their efforts to prove that this material is the real rust resisting material they claim it to be. A large share of the published work, which contains results from tests closely approaching actual service conditions, has been done by Mr. D. M. Buck—a strong advocate of copper-bearing steel ("Copper in Steel, the Influence on Corrosion," *Journ. Ind. and Eng. Chem.*, June, 1913; Buck and Handy, "Research on the Corrosion Resistance of Copper Steel," *Journ. Ind. and Eng. Chem.*, March, 1916). The opposing side appears mostly in discussion of these and other papers, and appears to be taking a defensive stand. The impression gained by the writers, from reading the available published evidence, is that copper-bearing steels do possess rust-resisting properties and are superior to any iron or steel now on the market.

Likewise, the influence of mill-scale upon the corrosion of iron is under discussion.

Friend, for instance, states that "traces of oxides upon the surface of metals are powerful stimulators of corrosion" ("The Corrosion of Iron and Steel," p. 251).

A. Sang says:—Black oxide only protects provided it is continuous and firmly anchored to the iron (Bower-Barff, &c.); as mill-scale, which is loose and fissured, it is detrimental, the iron in contact with it and exposed rusts about 50 per cent faster" ("The Corrosion of Iron and Steel," p. 81).

Aston and Burgess find "that mill-scale had an accelerating effect for an atmospheric test and a retarding action for a fume test." Further they state that "there is no doubt that the protective property of mill-scale is dependent upon its physical properties, continuity, &c." ("The Rate of Rusting of Iron and Steel," *Eighth Int. Congress of Applied Chem.*, xxvi., 453).

G. C. Whipple and M. C. Whipple tested steel, ingot iron, and wrought iron with mill-scale, and with mill-scale removed, and obtained erratic results, but, generally speaking, the rusting was slightly greater in the case of the metals from which the mill scale had been removed than in the cases of the metals on which the mill-scale had been left. They state, however, "that the best remedy to protect steel from pitting is to remove mill-scale" ("Mill-scale as a Cause of Corrosion," *Eighth Int. Congress of Applied Chem.*).

Back and Handy in their latest paper ("Research on the Corrosion Resistance of Copper Steel," *Journ. Ind. and Eng. Chem.*, March, 1916) state "at the time of exposure of the full-sized corrugated sheets careful notes were taken concerning the physical appearance of the sheets as affected by the amount of mill-scale which was present, and as to whether they were outside or inside in the pick. During the progress of the test this feature was carefully watched, and the time of ultimate failure of sheets whose surfaces were comparatively free from mill-scale was compared with others of the same grade, whose surfaces were well covered with mill-scale. From these observations we concluded that the influence of this original surface oxide is slight, and is lost in the early stages of rusting, for no difference in final failure could be noticed."

One thing, however, in regard to many tests that have been made up in the relative corrosion of iron and steel, is that in so far as the ultimate consumer is concerned, they are not of the greatest value, since many times only two or three materials were compared, or the materials were made especially for test, and cannot be obtained in com-

mercial quantities. Such tests do not carry the most weight since they do not have the air of disinterestedness that exist in the case of materials purchased upon the open market. In fact, one of the arguments of the pure iron advocates is the objection to "special tests" and the demand of basing comparisons upon service tests only.

In view of the fact that no results had been published of a complete test on commercial materials, it was deemed desirable to make a test containing all the types of iron and steel that could be obtained.

Some of the kinds of materials that are commonly used for structures, exposed to atmospheric corrosion, are:—

1. Steel.
2. Puddled pure iron.
3. Commercially pure iron.
4. Copper-bearing steel.
5. Cast iron.

This paper deals with the first four classes.

Accordingly there were obtained upon the open market the following materials in the form of black sheets of 26 gauge:—

1. Bessemer steel.
2. Open hearth steel.
3. Charcoal iron.
4. Commercially pure iron.
5. Commercially pure iron.
6. Copper-bearing iron.
7. Copper-bearing steel.
8. Copper-bearing Bessemer steel.
9. Copper-bearing open-hearth steel.

These materials analysed as follows:—

	Copper.	Manganese.	Carbon.	Phosphorus.	Sulphur.	Silicon.
1.	Trace	0.300	0.01	0.087	0.054	—
2.	Trace	0.413	0.01	0.079	0.041	—
3.	0.044	0.031	0.01	0.050	0.024	0.020
4.	0.016	0.028	0.01	0.009	0.025	—
5.	0.028	0.009	0.01	0.006	0.024	—
6.	0.237	0.006	0.01	0.004	0.054	—
7.	0.181	0.100	0.01	0.003	0.027	—
8.	0.256	0.315	0.08	0.092	0.046	—
9.	0.268	0.387	0.01	0.052	0.024	—

Before starting a work of this character, which involved quite some labour, due consideration was given to the methods of testing and in particular to those methods about which there is some difference of opinion. Questions arose concerning the desirability of a previous heat treatment, and the necessity and means of removing mill-scale previous to testing.

Opinions differ as to whether samples of iron should be tested just as received, or whether all test-pieces should receive some treatment so that the physical properties will be as nearly identical as possible. One author contends that samples should be tested as purchased, since the material that the samples represent will be used just as purchased. On the other hand, there are those who contend that all samples tested should have as nearly the same treatment as possible. They suggest, therefore, that the test-pieces be annealed at the same temperature and that mill-scale be removed.

It would seem that the method used for testing should depend upon the results to which the data is to be put. If the results are intended for the ultimate consumer the material should be tested just as purchased, since this is the condition that it is used by the ultimate consumer. On the other hand, if the data is for scientific purposes, such as determining the effects of various elements in the material, all variables other than the ones under investigation should be removed if it is possible to do so.

However, to make the work as broad and as complete as possible, it was decided not to limit the test to one method, but to try out both ways and to determine the relationship between the two.

Since part of the specimens were to have the mill-scale removed, the question arose as to what method should be used for removing this scale. In previous published work, very little has been said about the method of cleaning test specimens. When stated, however, it has usually been done by mechanical means, such as filing or grinding, or by chemical means such as acids. Experiments were therefore conducted on the effects of methods of removing mill-scale upon the subsequent corrosion. The results of these experiments have already been published (E. A. Richardson, "The Effect of Pickling on the Corrosion of Iron," *Met. and Chem. Eng.*, xii., 759). It was shown in this paper that methods of cleaning by the use of chemicals had a profound effect upon the rate of corrosion, especially on tests of short duration.

In the contemplated test a clean iron surface was necessary in which the surface iron was in the same physical and chemical state as the iron beneath the surface. It was therefore decided that removal of the mill-scale by pickling in sulphuric acid, thorough washing with water and drying, and subsequent removal of the surface iron with fine emery cloth would give a surface that was identical with the material itself.

The question also arose as to the method by which corrosion was to be estimated. There is a choice of methods to determine the rate of corrosion. One method commonly used is to determine the loss in weight after exposure for a given length of time and considering this loss as an index of corrosion. Another method is to allow the test specimens to corrode until failure occurs, and to take the length of time as an index of corrosion. Inasmuch as there is some question as to the reliability of the "loss in weight" method, it was thought best to continue the test to the failure of the specimens.

This made it necessary to decide upon some standard condition at which failure could be considered to have taken place. Evidently, failure should not be taken at a point when the iron has completely rusted away or even when it has almost disintegrated, since any sheet iron in service would be of no value long before such a condition obtained. The point of failure selected was when the sheet iron was in such a condition that it could be seen to be perforated when the rust was removed by gentle tapping with a blunt object, such as a file or nail. By using one specimen of each kind of material as a test piece that was tapped and examined at intervals of about two weeks, a close approximation to the time of failure could be obtained. Thus the other specimens were not molested until the latter part of their useful life and the effects of tapping were practically eliminated from the results. By this method it is believed that the life of each material was obtained to within an error of three or four weeks. The sheets of 26 gauge iron were accordingly prepared for test by cutting into pieces 5 in. by 8 in. (12.7 cm. by 20.3 cm.) For the test on the material as received ten pieces of each kind of iron, that was found by measurement to be of standard thickness, were used. For the test on the prepared material a number of pieces of each material were annealed at a red heat and then cleaned by the method already described. Great care was taken to give all of these test pieces exactly the same treatment. Ten of the prepared specimens of each material that were found by measurement to be of the same thickness were taken for test. These prepared pieces were of practically the same thickness as the "as received" samples tested, due, no doubt, to the extreme thinness of the mill-scale.

On account of the precautions taken as regards uniform thickness of materials, the method of estimating failure, and the method of cleaning surface, it is believed that the test should be comparative.

All samples were then placed securely in a wooden rack, and exposed to the weather May 24, 1914. The atmosphere was what might be described as a semi-country one and cannot be taken as at atmospheric acid test.

At the very start a marked difference was noted in the

character of the rust formed on different materials. Whereas, on the Bessemer and open-hearth steel samples, the rust was of a yellowish red colour and became loose rapidly, the rust on the others was dark red in colour and much more adherent. This adherent state seemed to reach its maximum in the copper steels, where the rust was very dark and fine grained.

The life of the different materials tested is given below; each figure being an average of ten test pieces, and represents the time for failure in days:—

	Material as received.	Material annealed and surface cleaned.
1.	348	363
2.	357	381
3.	615	558
4.	598	437
5.	675	467
6.	743	601
7.	1200	1200
8.	(estimated)	(estimated)
9.		

From visual observations at this time there appeared to be little difference between pure irons with or without additions of copper.

At the present writing the three samples of copper-bearing steel are still in good condition. The rust is still adherent and the underlying metal is still intact. The life of these steels has been estimated at 1200 days, which figure the writers believe is very conservative.

These specimens are still exposed to the weather, and will be until failure occurs.

Conclusions.—Taken as a whole the results indicate that copper-bearing steels are, without doubt, decidedly superior to any of the other materials tested. The remaining materials may be divided roughly into two classes, one class including the ordinary steels (Bessemer and open-hearth), and the other class the commercially pure irons and the copper bearing irons. Charcoal iron is classed with the pure irons. We have obtained results in another test which would indicate that the resistance of wrought iron to corrosion is due to the purity of its iron and not to slag inclusions. In addition it was noted during the present test that charcoal iron appeared to corrode in very much the same way as pure iron.

In regard to the steel-iron question it is noted that the pure irons (including charcoal iron) are superior to steel. It is believed that this superiority is due to the purity of the iron or to some combined effect of manganese and copper.

The results obtained in regard to the effects of mill-scale do not agree with the results obtained by others. They indicate that with steels which rust rapidly, mill-scale is a stimulator of corrosion. On the other materials tested the mill-scale has exerted a protective action. We have no explanation for this.

The important feature of the results, however, is that it substantiates the claim made in several other publications that the addition of copper to steel in amounts of about 0.25 per cent causes a remarkable increase in its ability to resist atmospheric corrosion. In the present test the addition of about 0.25 per cent copper to Bessemer or open-hearth steel has resulted in an increased resistance of 300 or 400 per cent.

The addition of copper to pure iron also results in an increased resistance to corrosion, but to no such an extent as the addition of a similar amount to steel. The addition of about 0.25 per cent copper to a commercially pure iron results in the useful life being increased by about 20 per cent. This figure was arrived at by comparing the average life of irons Nos. 3, 4, and 5 with No. 6.

We have been unable to determine the reason for this effect of copper in reducing corrosion. It is believed, in view of the fact that the copper exerts a greater influence in steel than in iron, that it must be due to the combined presence of copper and manganese, since the chief dif-

ference in the iron and steels under consideration is in the manganese content. It may be that the copper eliminates a harmful effect of manganese, or it may be that it is some combined effect of these two elements that acts as a protection to iron. The writers are inclined to believe that it is the latter course.

This conclusion the writers believe is also confirmed by the results of other observers. Mr. D. M. Buck ("Recent Progress in Corrosion Resistance," *Am. Iron and Steel Inst.*, May, 1915; also pamphlet, "K-yestone Copper-bearing Steel," American Sheet and Tin Plate Co.) tested several kinds of sheet irons and steel by exposing pieces 2 in. by 4 in. (5.08 cm. by 10.16 cm.), 27 gauge, to the atmosphere in a mill yard at McKeesport, Pa., and found the loss in weight after eleven months to be as follows:—

No.	C.	Mn.	S.	P.	Si.	Cu.	Loss. (a)
E...	0.04	0.30	0.043	0.065	—	0.31	2.65 (b)
V ..	0.04	0.39	0.078	0.114	—	0.31	2.75 (b)
Z ..	0.04	0.43	0.049	0.099	0.011	0.25	2.83 (b)
D ..	0.06	0.50	0.037	0.016	—	0.26	2.94 (b)
C ..	0.06	0.33	0.035	0.018	—	0.25	2.96 (b)
H ..	0.042	0.16	0.024	0.003	—	0.21	3.05 (c)
O ..	0.027	0.07	0.033	0.007	—	0.09	3.31 (d)
W ..	0.049	0.05	0.043	0.005	—	0.10	3.72 (e)
J ..	0.022	0.03	0.031	0.006	—	0.034	4.17 (e)
I ..	0.03	0.06	0.013	0.052	0.039	0.07	4.26 (e)
Y ..	0.04	0.45	0.046	0.099	0.006	Trace	6.94 (f)

(a) Loss given in ozs. per sq. ft.

Condition of Test Pieces after Exposure.—(b) No holes.

(c) Few holes in 2 pieces. (d) Few holes in 4 pieces.

(e) Many holes in all pieces. (f) Only a lace work of steel left.

Similar results were obtained upon tests made at Scottdale, Pa., and in McKeesport city water. These tests indicate that copper even up to 0.10 per cent added to low manganese materials increases their resistance to corrosion but little. Ordinary steels containing about 0.40 per cent manganese but no copper are very poor as regards resistance to corrosion, but additions of copper to such steels result in a greatly increased resistance. A maximum resistance is reached with about 0.25 per cent copper. These results were also confirmed upon full-sized sheets of the same materials, and in the above cited papers several excellent photographs are given.

The writers believe, in view of these results, that the resistance of pure iron to corrosion could be increased by the addition of both manganese and copper, and that additions of manganese to pure iron or steel, even up to 3 or 4 per cent, or more, with a corresponding increase in copper to produce a maximum effect should give a material more resistant to atmospheric corrosion than the copper steel now on the market.

Also some interesting results might be obtained by substituting for manganese in copper-bearing steels or irons, chromium, vanadium, tungsten, or molybdenum.

Summary.

1. Copper-bearing steels are decidedly superior to pure iron, steel, or charcoal iron.
2. The addition of copper to pure iron increases its resistance to corrosion, but to no such extent as similar additions to steel.
3. Charcoal iron and pure iron are superior to steel as regards resistance to atmospheric corrosion.
4. Charcoal iron is very similar to pure iron in its resistance to corrosion.
5. Copper is believed to decrease corrosion due to some mutual influence of manganese and copper.
6. The additions of large amounts of manganese and copper to pure iron or steel are suggested as well as additions of copper-chromium, copper-vanadium, copper-tungsten, or copper-molybdenum.
7. Mill-scale stimulates corrosion in rapidly rusting materials, and retards it in slowly rusting materials.

STUDIES ON THE ORIGIN OF MISSOURI CHERTS AND ZINC ORES.*

By G. H. CON, REGINALD S. DEAN, and
V. H. GOTTSCHALK.

(Continued from p. 54).

Colour.

ALL attempts to explain the colour of the jasperoid have appealed to the presence of organic matter, although Bain suggested that a part of it might be due to the presence of iron. Because of the ease with which colloidal solutions of the sulphides of lead and zinc can be formed, the ease with which solutions containing compounds of these metals can penetrate colloidal silica, and the close relation of the jasperoid to these minerals, the writers conceived the idea that the colouring matter of the chert might not be due to the presence of organic matter as hitherto supposed, but to some compounds of the associated metallic elements.

A study of the published analyses (Nos. 1, 2, 3, and 4, as shown in Table I.) and descriptions failed to show that the amount of organic matter had been carefully determined. The facts that the jasperoid turned white on being heated or upon weathering, and that the microscope showed that some specimens contained films and irregular fragments of what appeared to be organic matter are considered adequate proof of its presence in sufficient quantity and of its importance as a colouring agent.

Referring to the analyses of jasperoid herein published shows that the amount of organic matter in Nos. 1, 2, and 3 could be at most but a fraction of a per cent, as indicated by No. 5, the only sample in which an actual determination has been made. Even in No. 4, in which the amount of organic matter is reported as "large," if allowance is made for the undetermined substances, it could not exceed 2 per cent, and probably would be very much less. It is evident that this amount of organic matter would be unable to produce such a marked coloration unless it was asphaltic in nature and occurred as a thin coating about the grains. This is the condition outlined by Smith and Siebenhal, who say (*Folio* 148, p. 13, U.S. Geol. Survey, 1907):—

"Bitumen . . . is an almost constant constituent of jasperoid. . . . Between the grains of quartz is a variable but everywhere small amount of bitumen in brownish films."

Examinations of thin sections show that there is a slight brownish film surrounding many of the quartz grains in some sections. This is not uncommon in light coloured cherts. For example, it is more abundant and characteristic of the Grand Falls chert, which is white or light grey in colour, than of the jasperoid. Sample No. 5, when finely powdered and leached with acetone, chloroform, or petroleum ether, failed to show the presence of asphaltic material.

The more complete analyses, Nos. 5, 6, and 7, show the presence of lead, zinc, copper, and iron. In order to test the colouring effect of sulphides, a 0.02 per cent of lead (the amount shown to be present by the above analyses) in the sulphide form was introduced into an agar agar sol and H₂S passed in. The resulting gel was black, much darker than the jasperoid. A mixture of colloidal silica and colloidal lead sulphide was treated with Ca(HCO₃)₂, resulting in the two substances being thrown down together as a black gel. A powdered sample of jasperoid was strongly heated until most of the colour disappeared; and as the colour was restored by treating with H₂S, even in an acetic acid solution, it indicates that some of the colour at least is due to PbS and CuS. It thus seems evident that the dark colour of the jasperoid is due to the presence of sulphides, and that these probably exist as a solid colloidal solution with the silica.

* Bulletin of the School of Mines and Metallurgy, University of Missouri.

TABLE I.—Analyses of Jasperoid.(a)

	No. 1.	No. 2.	No. 3.	No. 4.	No. 5 (b)	No. 6.(b)	No. 7.(b)
SiO ₂	95.77	97.33	94.72	95.26	—	98.32 (c)	97.07 (c)
Al ₂ O ₃	—	—	—	0.57	0.949	0.37	1.05
Fe ₂ O ₃	1.84	1.89	4.00	None	(d)	0.40	0.53
FeO	—	—	—	0.69	(d)	—	—
MnO	0.24	0.09	Trace	0.05	0.098	Trace	Trace
CaO	0.54	0.11	1.18	0.25	0.228	0.37	0.51
H ₂ O and K ₂ O	—	—	—	—	—	0.69	0.99
H ₂ O	1.17	0.77	—	—	—	(c)	(c)
TiO ₂	—	—	—	—	0.070	0.06	0.04
MnO	—	—	—	None	None	Trace	Trace
CO ₂ (carbonate)	—	—	—	—	0.076	(c)	(c)
Organic matter	—	—	—	Large	0.179	(c)	(c)
Pb	—	—	—	—	0.022	0.016	0.02
Cu	—	—	—	—	0.015	0.01	0.014
Zn	—	—	—	—	0.241	0.01	0.008
Ni and Co.	—	—	—	—	0.001	Trace	Trace
	99.56	100.19	99.90	96.82	1.879	100.246	100.232

(a) Sample No. 1, from the Joplin district, exact location not noted; Nos. 2 and 3, from Galena, Kansas; No. 4, from Oronoga Circle Mine, near Oronoga, Mo.; No. 5, from Lanyon Mine; No. 6, from Ice Plant Mine, near Webb City, Mo.; and No. 7, from Bullfrog Mine, near Chitwood, Mo. Samples Nos. 1 and 2 were analysed by L. G. Eakins, U.S. Geol. Survey, and No. 3 by the St. Louis Sampling and Testing Works (see *Trans. Am. Inst. Min. Eng.*, 1893, xxii., 196). Sample No. 4 was analysed by George Steiger (see "Twenty-second Annual Report U.S. Geol. Survey," 1901, Part II., 121). Sample No. 5 was analysed by R. S. Dean, Missouri School of Mines and Metallurgy; and Nos. 6 and 7, by R. P. Rinker, Missouri Bureau of Geology and Mines.

(b) Analyses each made on 100 grm. sample. Silica was removed by treatment with HF. Lead and copper

were precipitated by H₂S. Lead was weighed as PbSO₄. Copper was determined electrolytically. Iron and aluminium were precipitated in filtrate and re-precipitated five times. Fe₂O₃ and Al₂O₃ were weighed together in aliquot parts. Fe was determined in another part, and Si in another. Carbonates were determined by evolution in a Corliss bulb and absorption with KOH. Organic matter was determined in a 10-grm. sample with chromate, wet combustion. Zinc was precipitated in formic acid solution as sulphide and weighed as phosphate. Nickel and cobalt were precipitated as sulphides and weighed electrolytically. Calcium and magnesium as usual.

(c) Silica and volatile matter determined together (see SO₂).

(d) Iron not determined, as sample was crushed in steel grinding machine.

In reference to the Peculiar Markings of the Cherts of the South-west Missouri Zinc District.

The cherts (excluding the jasperoid) of the south-west Missouri zinc district are all more or less characterised by peculiar markings, which have been well described by Smith and Siebenthal as follows (*Folio 148*, U.S. Geol. Survey, 1907):—

"Here and there the chert contains small scattered dark coloured, though still siliceous, spots or areas which are rounded, oval, or irregular in shape, some of the rounded spots being half-an-inch or more in diameter. Most of these areas are zoned, usually with a dark grey nearly jasperoid-like nucleus with sharp boundaries, surrounded in many instances by a light grey sharply marked zone that is, as a rule, nearly the colour of the main rock. This in turn is bordered by a zone of nearly white chert approaching cotton flint, this outer zone being commonly narrow, with an indefinite margin. While such spotting is not limited to any particular horizon, it appears to be the most abundant in the chert of the sheet ground, forming one of its marked characteristics."

Some dark spots in the grey chert have no surrounding rings, but the majority of them are separated from it by a single narrow band, lighter in colour than either. In some cases as many as six bands about a single dark centre have been counted, and it is probable that even this number is sometimes exceeded. In such instances the marking consists of a dark nucleus surrounded by light and by dark bands, the former of which are usually lighter in colour than either the centre or the unaltered chert, while the latter are intermediate between the two.

At first one receives the impression that the common case in which a dark centre is surrounded by a bleached

zone has probably resulted from a concentration of the colouring matter by crystallisation in the nucleus at the expense of the surrounding area, analogous to a garnet, the development of which in a schist may result in the formation of a light area about the garnet due to the leaching out of the iron. So far as we are aware, such opinions as have been expressed concerning the cause of these chert markings have been of this nature. Directly on this point Smith and Siebenthal say (*loc. cit.*):—"As shown by the microscope, the spotting is due to recrystallisation of the chert, and is in places accompanied by more or less solution, both in the nucleus and in the centre zone."

This marking is notably well developed in the Grand Falls chert, as is shown in the A.W.C. sheet-ground mines two and a-half miles west of Joplin, a study of which, together with other occurrences, has led to a conclusion entirely different from the above. It is thought that the dark centres or nuclei have not been formed at the expense of the surrounding material, but that they are invariably of different age, and perhaps of different origin, and represent direct contributions of jasperoid as fillings in small cavities and pores of the older grey chert. The relation of the main mass of jasperoid to the dark nuclei is shown in some cases by a continuous connection between the two along a fracture or enlarged pore, in others by the fact that the nuclei consist of an intimate mixture of the black chert and sphalerite, and in all cases by their exact similarity.

The concentric bands are of three types—grey bands of unaltered chert between lighter and darker areas; lighter coloured bands of "cotton" chert, which have resulted from the weathering of the grey chert; and dark bands which have been formed by the introduction of jasperoid material into more or less circular areas in which the chert

possessed exceptional porosity (usually "cotton" chert), a condition very typical of weathered cherts.

The weathering of chert has been described by Schmidt as follows ("Geol. Survey of Mo.," 1873-74, vol. i.):—"In many places the solid chert undergoes a change and passes into a soft porous variety. . . . The change always begins from the outside of the piece or from small crevices and cavities. . . ."

Smith and Siebenthal (*loc. cit.*) say:—"Cotton" flint, as seen under the microscope, contains many small cavities and shows on the whole a greater amount of recrystallisation."

We would add to the above quotations the statement that in all cases where silica has been deposited in the colloidal form, either as a filling in an opening or as a replacement of limestone, there tends to be developed rather pronounced textural (and perhaps chemical) differences in concentric layers. This condition results in certain of these layers weathering or disintegrating more readily than others, so that alteration tends to produce concentric bands of greatly different porosity. It is from the impregnation of these more porous layers that the dark circular bands have resulted.

As seen in the A.W.C. mines, the Grand Falls chert is considerably brecciated, the pieces ranging in size from small fragments up to those which are a number of feet across. The greatest dimension of by far the majority of them is, however, less than a foot. These have all been cemented together by the black chert or jasperoid and by the sulphide minerals, mainly sphalerite, with some galena and a barely discernible amount of marcasite, and show a very marked white band from one-half to three inches wide about their borders. The only exception to this banding is found on some pieces which are banded on but three sides, indicating that the fracture on the fourth side is later than the weathering and earlier than, or contemporaneous with, the introduction of the jasperoid and ore. In all cases where the jasperoid comes into contact with well bleached grey chert, the outer one-sixteenth to one quarter of an inch of the latter is dark or black, showing the introduction of the black chert into the pore spaces produced by weathering.

This proposed weathering of the cherts of the Boone formation before the introduction of the ore and associated substances is in perfect accord with the geologic history of this formation and area. During the considerable intervals of time represented by the unconformities between the Boone and the Cartersville, and the Cartersville and the Cherokee formations, there was a considerable erosion on the Boone, an almost complete removal of the Cartersville, and the water table was in general lower than at the present time. Even before the deposition of the Cartersville, fifty to one hundred or more feet of the Boone had been removed in places, sinks and underground drainage courses had been formed, and solution had reached a stage where slump and brecciation of the rocks had resulted.

If, then, these markings of the cherts have been brought about as outlined above, it should follow that they should be limited to areas which show signs of mineralisation, and that they should in themselves be evidence of sulphide minerals having been carried in solution and of the possibility of deposits of economic importance occurring in their vicinity.

SULPHIDES.

Carried as Colloids.

The readiness with which sulphide hydrosols can be formed, as outlined above, and the common occurrence of sulphides in limestone, where in many cases the amount of organic or reducing matter is so small as apparently to preclude the possibility of their formation by the reduction of sulphides, have suggested the possibility that in some cases they are transported as sulphide hydrosols and precipitated, like other colloids, by electrolytes, commonly $\text{Ca}(\text{HCO}_3)_2$.

It is recognised that in most cases suspensions can be

made from metallic sulphides if the degree of subdivision is sufficiently great. Freshly precipitated sulphides are usually in this state, and can then be readily put into suspension if free of any electrolyte. All of the theories of origin of the sulphide minerals of the South-west Missouri zinc district proposed in recent years agree that before the main concentration of the lead, zinc, and iron sulphides were disseminated through some sedimentary formation in a finely-divided state, having formed as a chemical precipitate from the sea-water. Thus Buckley and Buehler ("Mo. Bureau of Geology and Mines," 1905, vol. iv., 86) speak of the lead and zinc minerals as being "minutely disseminated." This, if true, provides ideal conditions for the sulphides to be carried as colloids in the absence of a strong electrolyte, and perhaps in the presence of an electrolyte, if suitable peptizing agents are present.

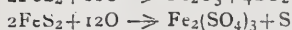
Lead and zinc sulphide colloidal solutions are readily formed in the laboratory under conditions which may be found in nature, but a colloidal solution of FeS_2 has never been prepared. It may be that this difficulty is purely a mechanical one, and can be overcome. The difficulty experienced with FeS_2 might lead one to think that a colloidal theory of transportation is not applicable, as it seems reasonable to assume that the three common sulphide minerals have been carried and precipitated in about the same manner. Yet one should remember that it is just this difficulty in connection with the transportation of these elements as sulphates and their reduction to sulphides that leads one to search for other methods of transportation and precipitation, for we cannot yet form FeS_2 from ferrous or ferric sulphate solutions under conditions that are applicable to natural deposits. It should be noted, however, that FeS_2 has been discovered deposited in the colloidal condition.

In order to confirm the formation and precipitation of sulphide hydrosols, colloidal solutions of lead, zinc, and iron (FeS) sulphides were prepared in various ways as outlined under colloids; but in general these were prepared by passing H_2S into a suspension of oxides or hydroxides, thus avoiding washing, the excess of H_2S being blown out with CO_2 . It was found that all of these sulphide hydrosols were precipitated by limestone and dolomite. The order of precipitation was found to depend upon many factors and was not determined. The principal factor, however, is the degree of dispersity, the less dispersed colloid being the more easily precipitated.

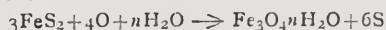
The Oxidation of Iron Sulphide.

Although iron sulphide is the most common of the sulphide minerals and is almost omnipresent in ore deposits, comparatively little is known concerning the chemical factors which control its alteration. Limonite, goethite, hematite, and sulphates of iron result in some manner from different alterations of FeS_2 . Limonite is the most common end product, but good pseudomorphs of red and even blue hematite after marcasite are not uncommon in Phelps and the adjoining counties of the Ozark region.

Some hypothetical alterations of FeS_2 :—



Seven equations have been written by adding sufficient oxygen and water to the FeS_2 to account for the products obtained, and may represent the result of a series of reactions. To the above list we would add—



These reactions show the alteration of mixed pyrite and marcasite to spinel, a magnetic iron oxide, a little SO_2 , and possibly other substances, an alteration which we find to be quite universal under certain conditions. It is probably true that under many conditions of chemical altera-

tions a number of different reactions may take place at the same time between the same substances, but just which of these reactions will take place or predominate is often affected by very slight changes in the conditions.

Experimental work and a study of altered specimens of FeS_2 has led to the conclusion that if plenty of water is present the common alteration to ferrous and ferric sulphate, sulphuric acid, &c., takes place, but that under conditions of insufficient moisture little or no sulphuric acid is formed, the chief alteration products being magnetite and free sulphur. Such a condition is found where specimens alter indoors as in a museum, or above the water table, as in the case of the sulphide bodies of the filled sinks of Missouri. Powdered pyrite and marcasite was washed with hydrochloric acid, with alcohol, and with ether, and placed in tightly stoppered bottles. After a lapse of about five years it shows a marked magnetic character, considerable free sulphur, and some SO_2 . It is quite probable that the magnetic material in such cases is formed as hydrous magnetite rather than as Fe_3O_4 , since much of it is removed by washing with dilute acids.

In order to test the general application of this reaction to the alteration of FeS_2 , many samples from the Southwest Missouri and the Wisconsin fields, as well as from local areas were examined, and almost invariably found to contain sulphur and magnetic material. Even sphalerite from these locations and from Leadville, Colo., and Jasperoid and Pennsylvanian shale from near Joplin, when ground in an agate mortar and tested with a powerful magnet, showed the presence of magnetic material. These facts indicate that this method of alteration of FeS_2 is common.

It is quite possible that this alteration may supply the long sought solution of the formation of hematite from FeS_2 , the hydrous magnetite formed changing over to this mineral. It is to these alteration products, existing in solid colloidal solution with the sphalerite, that we attribute the main colour of the latter.

To be continued).

CHEMISTRY AND PREPAREDNESS.*

LOOKING FORWARD TO TOMORROW'S NECESSITIES FOR INSURING COMFORT, PROTECTION, AND EVEN LIFE ITSELF, THROUGH THE EYES OF CHEMISTRY.

By HENRY P. TALBOT.

WHEREVER chemists have congregated for general discussions during the last five years it has been commonly remarked that "chemistry is at last coming into its own in this country." Since chemistry concerns itself with all that is embodied in the concept of matter, that is, everything which is recognisable by any of our senses, it would be more accurate to say that "the chemist is coming into his own." If the comforting phrase is further analysed it seems to mean that, as a people, and particularly in our industrial relations, we are coming to recognise what the chemist can and ought to do for us.

The enormous natural resources of our country, as well as our national traits, have led to an industrial development in which efficiency in office and sales departments, resulting in "big business," has contributed far more to financial success than manufacturing efficiency. We have wasted our substance, and, what is equally significant, our sources of energy, to a degree which, viewed in retrospect, is nothing less than appalling. But at last there has been an awakening! Competition has grown keener. The trivial loss is no longer insignificant, and by-products have saved the day for many a manufacturer. Increasing refinement of product is constantly demanded. Our table salt must be more than 99 per cent pure; the brown sugar

of our forefathers is no longer acceptable, and the refiner of sugars is now forced in his own interests to recover the last crystallisable product from molasses; steel is no longer a material ordered from a few general types, but under rigid specifications which embody the results of scientific researches and correspond with exactness to the demands which the steel must fulfil. There are few commodities or materials in use in the arts of which it can be said that a quality which met the demands of two decades ago is now regarded as sufficient, and in the great majority of instances this increased exactness has been accompanied by a lessening in the selling price.

We, as a people, are also properly awakening to an appreciation of what science, notably chemical science, can do in the public service. Although still too tolerant in many respects, we have enforced some degree of compliance with restrictions which will prevent or lessen the indiscriminate discharge of noxious manufacturing wastes into open watercourses, or the discharge of destructive or offensive gases into the atmosphere. It is not long ago that the Blackstone River in the vicinity of Worcester annually became a fairly concentrated acid solution of iron sulphate during each summer period of low water. Many other streams were rendered offensive by the discharge of wool-scourings in great quantities. But now many of the woollen mills are required, and all should be required, to work over this material within the mill, until the discharged waste is comparatively harmless, if not æsthetic in appearance. These, and thousands of similar problems, must find their solution in terms of chemistry, and where possible the waste product must be made a by-product and a source of profit, as is in some measure the case in the conversion of the objectionable wool-grease into toilet lanoline. If this is not practicable, then the expense of handling must be reduced to a minimum.

Greater, probably, than either or both of these factors in directing attention to chemistry and its possibilities of service has been the agitation in the interests of the conservation of our resources, a matter about which more will be said later in this paper.

The chemist, then, is "coming into his own" through the recognition by the captains of industry of the fact that, under prosperous conditions, the financial success of a manufacturing process will depend more upon the development of better methods of control, the elimination of waste, the working up of by-products, and the intelligent purchase of raw materials than upon skilled salesmanship and enormous output, however important these may also be. These improvements are, to a very large extent, the proper affair of the chemists and chemical engineer, and members of this profession are now being associated with all sorts of industries, even those not apparently chemical in character, and are given the standing of resident physicians, instead of being called in, as has too often been the case in the past, to administer the last sacraments to a process already moribund, or even to fill the office of undertaker.

The relation and services of the chemist to the enactment and administration of our state and federal "Pure Food Laws," and various other measures which tend to conserve health, to promote the improvement of our road-systems, and to gradually assure a larger degree of economy, through larger intelligence, in all departments of administration of Municipalities and States, attests the greater part which he now plays in public affairs.

Moreover, the chemist and his researches have achieved much for us that contributes to our comfort and happiness in a tangible way. Within the last few years synthetic dyes have been developed which exceed in brilliancy and durability the best of the natural dyes, artificial fibres which surpass in lustre the natural fibres; scents many times more powerful than natural perfumes; and synthetic drugs, the building up of which has effected profound changes in therapeutics, and alleviated much disease and suffering, besides putting new tools in the hands of the surgeon to diminish the pain and danger of his labours of

* Substance of a paper read before the Tuesday Club, of Newton, U.S.A., 1916.—From *Science Conspicuous*, vi., No. 4.

mercy and healing. Artificial substitutes for bone, ivory, horn, leather, resins, rubber, and celluloid are at hand, and this is but the prelude to greater achievements.

Great as has been the productiveness of chemistry during our long period of peace, the science has received a remarkable impetus and has attained unlooked-for prominence as a result of the great war. Indeed, it is frequently asserted that the present struggle is essentially a war waged between the chemists and the mechanical engineers of the different warring nations, with chemistry in the foreground. It has even been made a reproach to the chemist, by some pacifists, that some of his most beautiful conquests and proudest discoveries have been converted into agents of relentless destruction and terrible human slaughter. But to place the blame upon him because nitrocellulose, which was first used to heal wounds (collodion), and to advance the art of photography, is stolen away from these pacific purposes to make smokeless powder; or because carbolic acid, which revolutionised surgery, has been made the basis of the powerful explosive picric acid, is, as a writer (Bakeland) has said, no less unreasonable than to condemn written speech or language or the art of printing because they have been used to disseminate the vilest lies and damnable errors.

Within bounds, the assertion that the present war is one between chemists is true (as, indeed, it is true of all other wars since firearms were invented), and the statement by a British author (Martin) that "British chemists believe that if their Government had listened to them years ago the Germans would have been beaten in the early stages of the great war, and that thousands of lives would have been saved," and that "in the autumn of 1914 Germany was saved from a crushing defeat because she possessed the sense to encourage her chemists" can doubtless be substantiated.

In the discussions of preparedness in the public prints stress is naturally laid upon the training of men and upon the manufacture of arms and ammunition. These are, of course, vital; but it is no less essential that in the event of war our supply of foodstuffs should be adequate, and that the industries which supply our daily needs should not be seriously impeded.

Our supply of animal foods is dependent upon our agricultural prosperity, and our food supply is therefore measured by the ability of the farmer to maintain the productivity of his soil. In a country which still includes such large areas of untilled land, the problem is naturally less acute than in the countries of the old world. But the problem is still present, for it takes time to open up new land for cultivation, and in some of the sections of the United States, like our own New England, the taking of crops from the soil has proceeded for so many decades that the farmer is already dependent upon an artificial replenishing of the ingredients demanded for abundant plant growth. Let us look into this problem of sustenance somewhat in detail.

Land plants require for their growth, beside the carbon and moisture taken from the air and soil, nitrogen, phosphorus, and potassium in water-soluble form. The soils in which the plants grow are the product of the disintegration of rocks which, in turn, results from the action of the constituents of the atmosphere, particularly carbon dioxide and water. The soils contain the ingredients named above in varying amounts, but, if successive crops are taken from the same land, the local supply is gradually exhausted. Intensive agriculture then becomes necessary, and we resort to fertilisers made up of the soluble compounds of nitrogen, phosphorus, and potassium, in proportions which, when real intelligence is exercised, are adapted to the particular locality and crop. Of these ingredients we as a nation are especially fortunate with respect to phosphorus. The phosphate beds in the United States are of great extent and there is no "phosphate question" of importance to consider, since the demands of agriculture are not likely to be exceeded, even under conditions of war, and there is a further large potential

source of phosphates in some of the slags produced in the manufacture of irons and steels.

The Potassium Situation.

The situation with respect to potassium and nitrogen is less fortunate, and the "potash question," as it is commonly called, is one of vital importance.

Under normal conditions the potash market in the United States amounts to about 12,000,000 dols. annually. While this is small as compared with other products, its importance is relatively great. Some of our crops, such as beets, tobacco, and garden vegetables, require considerable amounts of potash for abundant growth, and nearly all require some potassium compounds. Potash salts are also used in smaller amounts in the glass, soap, and match industries. Recently it has become evident that potassium compounds are employed in the manufacture of certain explosives, although the exact nature of this demand is known only to the initiated.

Aside from the limited deposits of potassium nitrate in India and Persia, the whole world's supply of potash salts come from the famous Stassfurt deposits in Germany and the less-known but important Alsatian deposits. In 1909-1910 came the controversy between the American importers, the German Kali Syndicate (a selling agency under Imperial supervision) and certain independent producers, which finally led to diplomatic exchanges between the Governments. This served to focus attention upon the desirability of developing our own resources, and our predicament at the present time sufficiently emphasises this. It is difficult to estimate how much potash salts are in the hands of fertiliser manufacturers and brokers, but there can be very little as compared with the immediate need. Purchasers have gone as far as Borneo in the endeavour to obtain fresh supplies. Germany is not likely to release potash salts during the war, and even at its close it is probable that the price will be materially advanced, since these salts form one of her resources which can and will probably be made to shoulder a large part of the war burden. On this account the ultimate control of Alsace is of added interest to the world at large. There are deposits of uncertain value in Galicia, Spain, and Peru.

After the controversies of 1910, our Government and certain private interests began an active investigation into the possible sources of potassium compounds in the United States. These investigations show that, under certain conditions, the United States can produce within her own borders an amount of potassium salts much more than her needs, and that the limiting conditions are commercial rather than physical. In other words, under normal industrial conditions, these potash salts can be produced when the market price will warrant the necessary expenditure; for the extraction of these salts from the materials available in the United States is by no means as easy as from the European deposits, from which they can be obtained by simple solution and crystallisation.

Dr. Cameron, an authority on the subject, states that there are four notable sources of potash salts which have been under investigation. The first of these is *fel-par*. *Fel-par*, or orthoclase, a silicate of aluminium and potassium, is a constituent of many rocks, notably the granites. We have already seen that the potash naturally occurring in the soils comes from the disintegration of such rocks. The real problem, then, is to bring about an artificial disintegration consuming minutes rather than years. This has been shown to be practicable in itself, but the other disintegration products from *fel-par* besides the potassium compounds are not readily separated from them, and, without hand-sorting of the crushed rocks to concentrate the *fel-par*, which at once increases the cost of production to almost prohibitive figures for the present, the chemical separation is only partially successful.

A second potential source of potash salts is the salt deposits in the desert basins. Only one, Searle's Lake, San Bernardino County, California, affords much definite

hope. The brine in this lake carries from 5 to 6 per cent of potash salts, but it is impossible to separate these from other material by simple crystallisation and the cost of more complicated methods is enhanced by the difficulty of operation in the middle of a large desert. The best that is at present predicted from this source is that it may yield a small quantity of potassium salts, of uncertain quality, as a by-product in the manufacture of sodium bicarbonate, the cooking-soda of our households.

As a source of potassium sulphate, the salt most used in fertilisers, a deposit in Utah of a mineral known as alunite, having a general similarity in composition to the potash alum of commerce, is of considerable ultimate promise. After roasting this mineral, potassium sulphate can be leached from the residue by water. Inaccessibility to a market for the product is, under present conditions, a limiting factor, but it is stated that there is expectation that this material will be worked for potassium salts even after competition with those of European origin again comes into play.

Finally, much has been published regarding the interesting production of potassium chloride from the so-called Giant Kelps of the Pacific Coast. These sea-algae have the power of appropriating a considerable proportion of potassium from the sea-water, potassium chloride being always present in the ocean in small amounts. These kelp beds along the coast of the United States and Alaska aggregate more than 400 square miles. They lie within one marine league of the coast, and are therefore controlled by the States, not by the Federal Government. The plants have an average length of 100 feet, of which 30 to 70 feet streams along near the surface. A cutting of from 4 to 6 feet has no noticeable effect upon the harvestable area, and the cutting seems to produce a stooling effect, causing the plant to grow more thickly and heavily. It seems probable that several cuttings a year may be made without damage to the beds, and that these beds alone might be made to yield, under careful and judicious harvesting, some six or seven times the present normal demand of the United States, whenever the market price is such as to yield a sufficient financial return. The harvesting is relatively easy, although considerable losses were sustained before the great power of resistance of this heavy wet material was demonstrated. The greatest difficulty lies in drying this slimy mass, to cause the separation of the desired salts or as a preliminary to burning. The fuel expenditure in the drying process is very high. While the dried kelp is itself good fertilising material, the kelp-ash will probably command more of a market, if for no other reason than the high cost of transportation during the long haul to Eastern markets. The kelp will probably be most valuable as a source of pure potassium chloride, which is, in turn, used to manufacture potassium chlorate, an ingredient of almost all of the matches to-day, and, as recent events seem to show, an important war material.

It is evident, therefore, that potassium compounds must be carefully considered in plans for preparedness, from both the agricultural and munitions viewpoints. Because of the long-recognised agricultural importance of the potassium salts the Federal Government, through its Bureau of Chemistry and Bureau of Mines, has already devoted much time to a study of our national resources as just outlined. Dr. Cameron, in commenting on this, writes as follows:—

"While it is undoubtedly true that Governmental efforts can yet furnish assistance, there is a very serious doubt as to how far these efforts should be continued. The time seems to have arrived when the commercial interests should themselves squarely assume the tasks confronting them and the costs of what further experimenting is necessary. This they have been slow to do, but there is rapidly accumulating evidence that these interests are responding to the spur of necessity, and that sooner or later potash salts from American sources are to be put upon the market. An early cessation of the European war might

delay but can no longer stop the development of our potash resources."

While the view here expressed by Dr. Cameron may meet industrial needs, it seems evident that the Federal Government cannot afford to neglect to foster such a development as will ensure our ability to meet emergency demands such as are now upon us. Investigations should also be made to determine how far substitutes may, in emergency, be employed. It has already been found that, to some extent, the land plants can be made to assimilate sodium in place of potassium, and glass-makers have, under the stress of necessity, discovered that glasses can be made from soda (which in turn is made from table salt), which possess properties which were supposed to be attainable only through the use of the more expensive potash. Cut-glass, formerly made exclusively from lead and potash, is said to be a case in point. These discoveries, in two widely differing fields, are indicative of the conditions in applied chemistry in general.

Resources of Nitrogen.

The third ingredient of fertilisers, already named, nitrogen, and the "nitrogen question," because of its bearing upon both sustenance and defence, is, as a matter of preparedness, the most vital of all, not excepting the selection of a system for military training of men. Privation and helplessness, even humiliation, may well be the penalties attaching to indifference to this question to-day.

It is desirable to distinguish clearly between what is meant by free nitrogen and fixed nitrogen. We live in an ocean of atmosphere some six or seven miles deep, composed essentially of free oxygen and free nitrogen. This nitrogen gas exerts a pressure of about seven tons upon a single square yard of the earth's surface. Assuming an average figure for the content of nitrogen in living matter, it is within bounds to say that this amount of free nitrogen would correspond to 50 tons of living matter, provided only that the nitrogen can be harnessed for service.

Free nitrogen is an inert substance, and serves merely as a diluent of the oxygen of the air. When we describe its properties we at once begin to state the things which it will not do. But the very inertness of free nitrogen is probably explained by its intense activity towards itself. Free nitrogen is assumed to be made up of molecules of nitrogen, each containing two atoms of nitrogen united to each other, thus $N \equiv N$. In order that free nitrogen may become fixed nitrogen, that is, nitrogen in combination with other elements than itself, it is necessary for the molecule to be broken down into its separate atoms, since chemical changes take place between atoms of the elements, that is, $N \equiv N$ must become $2N$. This separation is hard to effect, and conversely once effected, it is hard to maintain. More specifically still, there is a tendency for a nitrogen atom which has been induced to enter into combination with other elements to release its hold on them and to recombine with another atom of nitrogen. Hence free nitrogen is stable and indifferent, while many nitrogen compounds are unstable. Some are violently so, and are, as we shall see, our explosives; others constitute vital components of our animal and vegetable food supplies and of our own bodily structures. The latter type disintegrates, for the most part, peacefully. It is, nevertheless, their tendency to thus disintegrate which gives them their food value. Free nitrogen taken into the lungs is exhaled unchanged; but nitrogen assimilated as food becomes for the time a part of the animal body, and passes out of the animal system in the excretions, in the form of new nitrogen compounds, formed within the body. These return to the soil, are acted upon by bacteria in the soil and converted into soluble nitrates, which then exercise manurial properties and are taken up by vegetation. The vegetable foodstuff is again eaten, assimilated, and the nitrogen compound again excreted. This is known as the nitrogen cycle, within which our lives seem to be set.

Aside from this supply of free nitrogen which resists efforts to convert it into fixed nitrogen, what have we at hand for use in our fertilisers, to sustain or intensify agriculture? We are restricted to soluble nitrogen compounds, essentially to compounds of nitric acid (the nitrates), and to the compounds of nitrogen with hydrogen (ammonia), and its derivatives, chiefly ammonium sulphate. The naturally occurring nitrates of sodium and potassium are now so valuable for their yield of nitric acid or potassium that, although they have of necessity been used in the past, ammonium sulphate is probably the substance of main significance for the future, so far as our natural supplies are concerned.

The commercial source of ammonia is chiefly that of a by-product in the manufacture of coke and coal-gas. When soft coal is heated in a closed retort or oven, volatile ingredients distil from it, made up of what we call coal-gas for illuminating purposes, coal-tar, and ammonia. The ammonia is collected in water, in which it is very soluble. The ammonia water thus formed is treated with sulphuric acid, and the ammonium sulphate crystallised from the solution. The annual production amounts to about 1,250,000 tons, but this is far less than the present demand, which will constantly increase. It is true that there has been an appalling waste of ammonia in the production of coke in the so-called bee-hive ovens, from which all the volatile products escaped into the air, but it is plain that even if this is reclaimed it will far from suffice in the future for agricultural needs.

A minor additional source of ammonia has been found in the cremation of garbage, and in procedures for the recovery of ammonia from water-gas.

How then can we tap the atmospheric reservoir for material to protect our food supplies?

The bacteriologist has shown us one way by which Nature accomplishes this object by demonstrating that certain bacteria which find a residence in the nodules at the roots of leguminous plants, such as clover, and alfalfa, are able to assimilate free nitrogen from the air, and convert it into some compound which the clover, &c., in turn can assimilate into their structures. These plants can, then, be employed as miniature fertiliser factories, *in situ*, for, if the plants are subsequently ploughed in, and undergo decay and oxidation at the hands of other bacteria, the resulting water soluble nitrogen compounds are taken up by the next crop. This is, to be sure, a partial relief, but obviously slow and insufficient.

But the chemist has discovered at least two commercially practicable procedures which are more rapid and significant. The first of these is the manufacture of cyanamide, a name which means but little to most of us. It is also known as "lime-nitrogen" and "*Kalkstickstoff*." This procedure has been made possible, in turn, by the development of the electric furnace. In these furnaces very high temperatures are attained by passing very heavy electric currents through the mass of reacting material, which, because of its resistance to the passage of the current, becomes highly heated, without the use of external fuel. It is similar in principle to the overheating of electric wiring by too heavy currents.

Calcium carbide, made in such furnaces from lime and coal, is familiar to us as a source of acetylene gas, when treated with water. If free nitrogen is passed over this carbide under suitable conditions, it combines with it to form what is called calcium cyanamide. This, in the presence of water, gives ammonia as one of the reaction products. The cyanamide can be also used directly as a fertilising agent.

Two features of this process require further attention. The nitrogen used must be nearly free from oxygen. Fortunately, methods are known by which such a separation of the two main constituents of the atmosphere can be brought about. Air can, to-day, be liquefied with ease, and the resulting liquid consists, of course, of a mixture of oxygen and nitrogen. This may be compared with the mixture of alcohol and water which we are accustomed to

use in winter in the radiators of automobiles. It is well-known that the alcohol "boils away" first from such a mixture, and the reason is that the alcohol is more volatile, that is, has a lower boiling-point than water. If we were to collect and examine the first portion of the vapour from such a mixture, it would be found to be nearly pure alcohol. Now nitrogen is more volatile than oxygen. Hence, if liquid air is allowed to evaporate, under regulated conditions, the nitrogen escapes first from that mixture, and such nitrogen corresponds to the alcohol above and is so nearly pure that it can be readily freed from remaining amounts of oxygen. This is, in mere outline, the way in which the free nitrogen is obtained from the atmosphere in quantity to-day, as a first step in the processes for its fixation. It is fundamental to the success of such processes as we are now considering.

The second point to be emphasised is that electrical energy is used as a source of heat, and, as is well known, water-power is usually the cheapest source of energy. This process has accordingly found its chief development in Norway and Sweden. It is stated that an English company is planning the application of 1,000,000 horsepower in Norway and Iceland, in addition to the 200,000 now in use in various places, for the production of the cyanamide. It is significant that not a single factory exists in the United States, although we have much available water-power.

The second chemical procedure for the "fixation of nitrogen" is the direct union of nitrogen with hydrogen to form ammonia. This has been developed in Germany by Prof. Haber and the chemists and engineers of the Badische Anilin and Soda-fabrik. The nitrogen is obtained in the way just described. The hydrogen is probably obtained by the electrolytic decomposition of water. The two gases do not readily combine, but under a great pressure of 3000 lbs. per square inch and at 500°C. they can be made to combine, in the presence of a catalyst, that is, a substance which merely by its presence increases the rate of a chemical change, its effect being sometimes compared to the lubricant on the works of a clock. Uranium is the substance supposed to be used in this case.

That this process is a commercial success is beyond question, and it is in part due to it that Germany has not long ago exhausted her supply of ammunition, for, by another process, involving the use of a different catalysing agent, ammonia and air can be converted into nitric acid, and without nitric acid not one of the explosives in actual use in peace or warfare could be manufactured.

The world supply of nitric acid has, until recently, been derived from natural nitrate beds, composed of sodium nitrate, located almost entirely in Chile and Peru. It is known as Chile saltpetre. There is some potassium nitrate in India. The nitrates can only be found in an almost rainless country, as they are very soluble in water.

Chile has an annual output of about two and a half million tons of nitrate. The United States takes from one-fifth to one-fourth of this output. It is estimated that about 50 per cent of the nitrate imported into this country is used for explosives, 25 per cent for the manufacture of nitric acid for other uses, and 25 per cent as fertiliser. It is, of course, very valuable for the last-named purpose.

Sir William Crookes, in his presidential address before the British Association for the Advancement of Science in 1898, dwelt with great earnestness upon the serious necessity for the development of processes which should enable us to obtain nitric acid from other sources, since the visible supply of natural nitrates seemed likely to be exhausted by the middle of the present century. The seriousness of the extreme localisation of these supplies finds forcible illustration in the present situation of Germany.

More than a century ago Cavendish pointed the way to what in point of time was the first commercial process for the production of nitric acid from the nitrogen in the atmosphere. He showed that nitrogen and oxygen, both,

of course, close at hand, will combine to some extent when an electric spark is passed through a mixture of the two gases. An oxide of nitrogen results from which, on contact with hot water, nitric acid is formed. The yield was very small and unpromising. Under the stress of approaching need this process was studied anew. It was found that by spreading out the electric discharge by means of electro-magnets the gases could be exposed to an electric flame several feet broad, and by a suitable and regular removal of the products of the change the yield could be greatly increased. Here, again, oxygen and nitrogen are readily available, but the generation of electrical energy at a figure which would permit of a possible competition with natural nitrates under normal industrial conditions would presumably require the use of water-power to drive the generators. The first commercial plant to operate under this procedure was built in 1902, at Niagara Falls, on the American side, by two American pioneers, Messrs. Lovejoy and Bradley, and to them belongs the credit of having furnished the first answer to Crookes's call of distress. In all probability they also laid the foundation for a development which has made it possible for Germany to challenge the world at arms. Why is this plant not in operation to-day? Simply because the authorities failed to take the slightest interest in the matter, and private capital was suddenly withdrawn. Abroad, however, the situation was different. In Sweden and Norway, with cheaper water-power, and upon the foundation of the experimentation of Lovejoy and Bradley, backed by plenty of capital in the hands of well-advised bankers, and aided by the co-operation of established industries, the "fixation of nitrogen" in the form of nitric acid has been greatly developed. The best known process is that of Birkeland and Eyde, based upon the principles just briefly outlined.

Directly or indirectly the Birkeland and Eyde process, and its modifications, has played a conspicuous part in Germany in the production of the required quantities of nitric acid, and must receive serious attention in our own country if we are to meet the future demands upon a peace or war footing.

Other procedures for the production of ammonia, in which, for example, the free nitrogen is made to combine with aluminium, and the resulting nitride is treated with water, the Surpeck process, are of potential importance, but must be passed by with this mere reference.

(To be continued).

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clxiii., No. 21, November 20, 1916; No. 22, November 27, 1916; No. 23, December 4, 1916. These numbers contain no chemical matter.

No. 24, December 11, 1916.

Oxidation of Coal.—Georges Charpy and Marcel Godchot.—When specimens of coal from central France are heated to 100° there is first a decrease of weight, due to the evaporation of water; at the end of about three hours desiccation is complete, and if heating is continued the weight gradually increases. The increase gradually lessens, and ceases after two and a-half or three months. At temperatures up to 150° the phenomenon is the same, but the rate of oxidation increases a little as the temperature rises. Above about 150° CO₂ is evolved, and loss of weight occurs. The calorific power of the oxidised coal is considerably reduced. The authors have studied the phenomena quantitatively with fourteen samples of coal from St. Eloy, Noyant, and Ferrières. They find that the loss of weight on heating for three hours to 100° is practically identical with the loss of weight on drying *in vacuo* at the ordinary temperature, and represents the

amount of moisture in the coal. The increase of weight produced by prolonged oxidation at 100° is about 3–5 per cent of the initial weight of the coal. The diminution in calorific power produced by oxidation at 100° amounts to 3–13 per cent. The amounts of ash and volatile matter are not appreciably altered by prolonged oxidation. Oxidation often occurs in coals stored in heaps, and even in the mine, so that the estimation of the value of a coal from its percentages of ash and volatile matter is liable to serious error.

New Effect Relative to Thermo-electricity and to the Thermal Conductivity of Metals.—Carl Benedicks.—From theoretical considerations the author has arrived at the conclusion that the deduction made by Drude from the law of Wiedemann-Franz is not admissible, and that the proportionality between the thermal and electric conductivity is due to the fact that when a homogeneous metal is heated unequally strong electric currents arise, and occasion a considerable transport of heat. He has investigated the subject experimentally, and has arrived at confirmatory evidence. He has found that the thermal conductivity of metals is not independent of the dimensions of the sample.

Grouping of the Lines of the Iron Spectrum under the Selective Influence of Thermal and Chemical Actions.—G. A. Hemsalech.—The lines in the iron flame spectrum can be grouped in three classes:—(i.). Lines emitted by the external flame of a Bunsen burner and reinforced in flames of higher temperatures. They are particularly sensitive to thermal actions. (ii.). Lines produced under the influence of chemical actions. They are very marked in the cone, but feeble in the flame. (iii.). Lines of the "supplementary" spectrum. The examination of the spectra reveals the existence of curious groups of lines in each of these three classes. These groups are composed of three, four, or more lines, the nature and distribution of which appear to be governed by some as yet unknown law. The groups of the first and second class are towards the red, and of the third towards the violet.

MEETINGS FOR THE WEEK.

- MONDAY, 12th.—Royal Society of Arts, 4.30. (Cantor Lecture). Town Planning and Civic Architecture," by Prof. Beresford Pite.
- Biochemical Society, 5.30. (In the Institute of Physiology, University College, London). "Investigations on Permeability of Plant Tissues," by W. Stiles and I. Jørgensen. "Effect of various Concentrations of Carbon Dioxide and Oxygen on the Permeability of Plant Tissues," by F. Kidd. "The Baumstark Phenomenon—The Expulsion of Water from Tissues through Exposure to Ether or Ether Vapour," by W. A. Osborne. "A Synthetic Methyltryptophan and its Behaviour in the Dog," by G. Barger and A. J. Ewins. "Nucleic Acid from Peat," by W. B. Bottomley.
- TUESDAY, 13th.—Royal Institution, 3. "Pain and its Nervous Basis," by Prof. C. S. Sherrington.
- WEDNESDAY, 14th.—Royal Society of Arts, 4.30. "Highways and Footpaths," by Lawrence Chubb.
- THURSDAY, 15th.—Royal Institution, 3. "The Mechanism of Chemical Change," by Prof. F. G. Donnan.
- Royal Society. "Structure and Development of the Tubular Enamel of the Sparidae and Labridae," by J. H. Mummery. "Distribution in Wheat, Rice, and Maize Grains of the Substance the Deficiency of which in a Diet causes Polyneuritis in Birds and Beri-beri in Man" and "Effect of Exposure to Temperature at or above 100° C. upon the Substance (Vitamin) whose Deficiency in a Diet causes Polyneuritis in Birds and Beri-beri in Man," by Harriette Chick and E. M. M. Hume.
- Society of Glass Technology, 4.30. (At the University, Western Bank, Sheffield). Collection of Specimens of Glass made by Mr. C. J. Peddle. "The Annealing of Glass," by F. Twyman.
- FRIDAY, 16th.—Royal Institution, 5.30. "Author's Dedications in the Seventeenth Century," by Very Rev. H. Hensley Henson.
- SATURDAY, 17th.—Royal Institution, 3. "The Mystery of Counterpoint," by H. Walford Davies, Mus. Doc.

THE CHEMICAL NEWS

VOL. CXV., No. 2586.

ON THE ACTION OF POTASSIUM PERMANGANATE AND THE METALS.*

(PRELIMINARY PAPER).

By Prof. WILLIAM FOSTER.

ON pp. 360—361 of the 1916 edition of his text-book entitled, "General Chemistry for Colleges," Alexander Smith discusses the more "active" ("nascent") state of hydrogen, and in order to show that the active state has no necessary connection with an immediately preceding act of liberation, the author suggests the following experiment:—"Three test tubes are filled with dilute, acidified potassium permanganate solution. Zinc dust, added to one, generates hydrogen and causes decolorisation. A little platinum black is added to the second, and hydrogen gas is led through this and the third. The contact action of the platinum enables the hydrogen quickly to reduce the permanganate, while the third portion remains unaltered."

In February last, while performing this experiment for my class in chemistry, I happened to observe that the portion of the very dilute permanganate solution to which platinum black was added began to fade in colour even before hydrogen gas was passed through it. This observation at once led me to conduct a large number of experiments with dilute aqueous solutions of potassium permanganate and many of the elements, and particularly the metals from gold and platinum to magnesium. Very pure potassium permanganate was dissolved in conductivity water, and N/100 and N/1000 solutions were prepared.

The experiments were conducted at room temperature. The general observation was made, that not only do all the common metals decolorise (reduce) acidulated solutions of potassium permanganate, but dilute neutral solutions of the permanganate are reduced as well, even by finely-divided platinum and gold.

The further general observation was made that, neutral solutions of potassium permanganate interact with the metals to form an alkaline solution, thus showing that potassium hydroxide is formed in every case.

While it has been known for a long time that certain of the metals in the elementary condition interact more or less readily with potassium permanganate in aqueous solution, no one was familiar with the generalisation, so far as I have been able to find out, that a neutral solution of potassium permanganate is reduced by all the common metals from the noble metals to the active metals, such as zinc and magnesium.

The greatest surprise of all was the rapidity with which mercury and the permanganate interact. Not only is the latter quickly decolorised, but the mercury is oxidised as well.

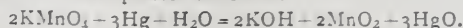
This observation was made originally by Giles (CHEM. NEWS, 1867, xv., 204).

In 1867, Giles published a paper entitled, "On the Action of Permanganate and Certain Metals." According to him purple permanganate first yields green potassium manganate, the latter then decomposing to form KOH and brown manganic oxide. The powder formed was said to be Hg₂O. Giles said that the permanganate appeared to exert a slight action on pure silver, but added that the solution had no action upon copper, even when kept at

100° C. for several hours. The editor of CHEMICAL NEWS added in a note that "neither magnesium nor aluminium exerts any apparent action on dilute permanganate of potassium in the cold."

In 1911, David Borar published a paper entitled "Some Reducing Actions of Mercury" (Journ. Chem. Soc., 1911, xcix., 1414).

He arrived at the conclusion that the interaction between mercury and an aqueous solution of potassium permanganate can be expressed as follows:—

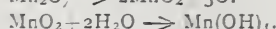
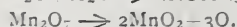
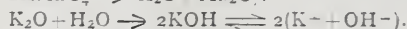


It is interesting to note that finely-divided silver reduce dilute permanganate solution rather quickly. Even hydrogen gas decolorises very dilute permanganate solution when passed for some time (V. Meyer and Recklinghausen, Ber., 1896, xxix., 2549, 2825). Antimony and tungsten reduce the permanganate quickly, but in case of the latter the solution is practically neutral. This suggests that tungsten is first oxidised and the oxide then interacts with KOH to form tungstate. Arsenic is very similar to tungsten.

The Mechanism of the Reaction.

Numerous experiments of a preliminary nature were conducted with a dilute solution of potassium permanganate and nearly all of the common metals, and it would appear from these experiments that the various reactions involved are fundamentally the same.

In the presence of a metal, potassium permanganate suffers reduction with formation of oxygen, potassium hydroxide, and most likely hydrated manganese dioxide—



In the case of certain metals, e.g., mercury, the oxygen converts the metal into an oxide, but such inactive metals as gold and platinum escape oxidation, and serve merely as catalytic agents in decomposing the permanganate. In some cases, certainly, green potassium manganate is formed as an intermediate product of decomposition.

More work along this line is contemplated by the writer.

Princeton, New Jersey, U.S.A.,
December 1, 1916.

THE NITRATION OF TOLUENE.*

By E. J. HOFFMAN.

THIS paper is the result of experiments made in the Bureau of Mines on the preparation of trinitrotoluene from toluene obtained in the manufacture of water-gas. There seems to be a rather prevalent view that so-called water-gas toluene is unsuitable for the manufacture of trinitrotoluene, because of the toluene containing hydrocarbons of the aliphatic series whose removal cannot be effected by the usual methods of purification. It was in anticipation of such difficulty that the present investigation was undertaken.

The investigation early showed that if the sample of water-gas toluene under investigation contained any aliphatic hydrocarbons they were present in negligible quantity so far as affecting nitration. Consequently, the investigation became a more general one, embracing the nitration of any good grade of toluene, and it was continued with a view not only of ascertaining the conditions under which the best yield of trinitrotoluene could be obtained from a sample in hand, but also of developing a method that might be capable of satisfactory industrial application to the nitration of any toluene of approximately the same degree of purity.

* Contribution from the Chemical Laboratory of Princeton University.

* From a technical paper issued by the U.S. Bureau of Mines. From the Chemical Engineer and Manufacturer, xxiv., No. 5

Ample justification for such an investigation is to be found in the incompleteness of published details with respect to methods already successfully applied in the industries. Although much valuable information was available in the literature on the nitration of toluene, the author was unable to select any method or combination of methods described that could be said to cover the whole problem in hand; nor were the data available sufficient to determine the relative merits of different procedures with respect to quantity and quality of yield of trinitrotoluene.

Technical Methods for Manufacture of Trinitrotoluene.

(NOTE.—For the sake of brevity the abbreviation "T.N.T." is used for "trinitrotoluene." Similarly "D.N.T." and "M.N.T." stand for "dinitrotoluene" and "mononitrotoluene").

Early Processes.—A trinitrotoluene having a melting-point of 82°C . was prepared in 1863 by Willbrand (5) by the action of fuming nitric and sulphuric acids on toluene. By the further nitration of dinitrotoluene, Beilstein and Kuhberg (9), in 1870, and Tiemann (10), in 1870, obtained similar products. In 1882 Hepp (15), by the action of very concentrated acids on paranitrotoluene and 2,4-dinitrotoluene, obtained a considerable quantity of a trinitrotoluene. Metanitrotoluene yielded by the same treatment β - and γ -trinitrotoluene.

Häussermann's Methods.—Häussermann (26), in 1891, described a technical method for the manufacture of trinitrotoluene (T.N.T.) which avoids the highly concentrated acids of Hepp. One hundred parts of paranitrotoluene was treated with a mixture of 75 parts of 91 and 92 per cent nitric acid with 150 parts of 95–96 per cent sulphuric acid. During the addition of the nitrating acids the temperature was maintained at 60 – 65°C ., after which the mixture was further heated at 80 – 85°C . for one-half hour. The yield of D.N.T. melting at 69.5°C . was approximately 130 parts. The latter was slightly heated, dissolved in 4 parts of 95–96 per cent sulphuric acid, and treated with 1.5 parts of 90–92 per cent nitric acid, after which the temperature was kept at 90 – 95°C . for four to five hours. The yield of T.N.T. (melting-point 79°C .) was 105 parts from 100 parts of D.N.T.; by recrystallisation a product having a melting-point of 81.5°C . was obtained.

Method of Vasquez.—Vasquez, 1911, described a method for the manufacture of T.N.T. from toluene in three stages, and gave details of apparatus and procedure in manufacture and refining. According to this method the spent acids (90 litres) from the preparation of D.N.T. are fortified with the required nitric acid, and added to an equal weight of toluene, with constant stirring and with cooling, to prevent a rise of temperature above 30°C . After standing six hours the resultant M.N.T. is separated.

The spent acid is regenerated by the use of sulphur trioxide, and mixed with a quantity of nitric acid equal in weight to the M.N.T. formed. The mixed acid is added as above to the M.N.T. at a temperature of 90°C . After six hours the product is cooled to -2°C ., and the spent acid is drawn off from the D.N.T.

For the third stage of nitration stronger acids are added to the molten D.N.T., raising the temperature to 92°C . After twenty hours the mixture is transferred to another vessel, and after four to five days the separated solid is washed with water and alkali, then refined by being washed with acetone and soda, and finally crystallised from alcohol.

Langenscheidt's Method.—A method devised by Langenscheidt to obviate the necessity of separating the D.N.T. from the spent acid after the conversion of orthonitrotoluene into D.N.T. is as follows:—500 kgrms. of orthonitrotoluene is dissolved in 1400 kgrms. of 100 per cent sulphuric acid, and warmed to 60 – 70°C . The mixed acid consisting of 700 kgrms. of 100 per cent sulphuric acid and an equal weight of 48°B . (94.09 per cent) acid is introduced in a thin unbroken stream. In the be-

ginning the reaction is violent and much cooling is required; as the nitration proceeds the heat evolved decreases. A fall in temperature indicates that the orthonitrotoluene has gone over into the second stage of nitration. All the mixed acid is gradually introduced, and the whole is slowly warmed up again until a further reaction takes place—the nitration of D.N.T. to T.N.T. The heat evolved in this stage of the nitration is not so great as in the first stage. If means of cooling the liquid are not used the temperature usually rises to 120 – 130°C . As soon as the temperature begins to fall the contents of the nitrating vessel are brought to 150°C ., and this temperature, or just as well a temperature of 120 – 130°C ., is maintained for about one hour. When the reaction mixture has cooled to 100°C . about 200 litres of water is added to increase the yield.

Langenscheidt's method for manufacturing T.N.T. from D.N.T. is as follows:—500 kgrms. of D.N.T. is placed in the apparatus and melted; the mixed acid consisting of 1125 kgrms. of oleum (20 per cent) and 305 kgrms. of nitric acid (48°B .) is slowly added at 70 – 75°C . When the addition of acid has been completed the contents of the apparatus are slowly and carefully warmed. The reaction begins at 90 – 100°C . and a temperature of 130°C . is reached, which is maintained for one hour, after which the products are cooled to 100°C . and treated as above with water.

The resultant T.N.T. separated cold by the method here indicated, or in the liquid condition, is forced into lead wash tanks containing water at 40 – 45°C ., and washed with steam till neutral. By crystallisation from a mixture of 9 parts of alcohol and 1 part of benzene a product is obtained that melts at 81 – 82°C ., and solidifies at 80.3 – 80.4°C .

Method of Vennin and Chesneau.—The following method of Vennin and Chesneau provides for the direct nitration of toluene to T.N.T. in one operation:—20 kgrms. of toluene is added slowly to a mixture of 80 kgrms. of 91–92 per cent nitric acid, 450 kgrms. of 93–94 per cent sulphuric acid, and 25 kgrms. of oleum (60 per cent sulphur trioxide) at 40°C . The mixture is then heated two hours at 80 – 85°C ., and three hours at 100 – 105°C . After the mixture has cooled the spent acids are drawn off, and the T.N.T. is crystallised from hot sulphuric acid and washed with hot water. The product thus obtained melts at 77 – 79°C . By washing with 95 per cent alcohol, or alcohol containing 10 per cent benzene, a product is obtained that melts at 81°C . The yield is given as 150 per cent referred to the toluene used.

Importance of available Alcohol.—As prepared by the methods described above the T.N.T. of desired purity is obtained by crystallisation from alcohol. If the necessary alcohol is available at a reasonable cost this procedure presents no difficulties, but if, for economic reasons, alcohol cannot be used it is necessary to proceed in such a way that crystallisation of the water-washed product is avoided. The direct nitration of toluene to dinitrotoluene yields, mainly, the 2,4 D.N.T.; but the product contains also 7–10 per cent of an orange-yellow oil known as "drip oil" (German "Tropföl" or "Binitropföl"), which investigation (11, 12, 16, 17, 19, 28, 30, 50, 53) has shown to consist of traces of orthonitrotoluene, about equal parts of meta and para M.N.T., the 2,4, 2,5, 2,6, and 3,4 D.N.T. 2,4,6 T.N.T., and either 2,3,5 or 2,3,6 T.N.T. In Germany this liquid affords a valuable and economical starting point in the manufacture of T.N.T. In Italy, however, by starting with a D.N.T.) product having a melting-point of 63 – 66°C ., a T.N.T. is prepared that without crystallisation from alcohol melts at a temperature only 1 – 1.5° lower than that required for the pure T.N.T.

Giua's Method.—Giua recently describes a method for thus preparing a high grade of T.N.T. Pure toluene, in a special nitration apparatus provided with a stirring device to keep the liquid constantly agitated, is nitrated with a mixture of nitric and sulphuric acids containing 18–22 per

cent nitric acid and 15–20 per cent water. To assure a satisfactory product, 1·5–1·8 times the theoretical amount of nitric acids must be used. The temperature of reaction must not rise above 110–120° C. By the use of the centrifuge or other mechanical means the drip oil formed can be removed sufficiently from the solid D.N.T. so that by washing well with water a product is obtained that melts at 63–66° C.

Subsequent nitration of this product is accomplished by treatment with anhydrous acid containing 18–25 per cent nitric acid, the ratio of toluene to nitrating acid being 1–4 or 1–5. The reaction begins at 60–65° C.; the temperature is regulated by cooling means so that it does not exceed 118–122° C. By treatment with the nitrating acid mentioned in the ratio of 1–2 the red oil removed from the solid D.N.T. yields at 66° product.

Method of Escalles.—Escalles has described in detail apparatus and methods for preparing the various nitrotoluenes, the following abstract being taken from his description:—

1. *Mononitrotoluene.*—The toluene (200 kgrms.) is introduced into the proper nitrating vessel, provided with a cooling and a stirring apparatus. The nitrating acids, 350 kgrms. of 66° B. sulphuric acid (specific gravity 1·84) and 225 kgrms. of 44·1° B. nitric acid (specific gravity 1·41), are added over a period of eight hours. The temperature attained in one hour (60° C.) must not be exceeded. After introduction of all the acid the operation is continued two hours longer, after which the mixture is allowed to stand over night. The spent acid is used over again for the preparation of the next lot of M.N.T., after addition to it of 150 kgrms. of 44·1° B. nitric acid. If the mononitrotoluene is desired for other purposes, isomers may be separated and purified. Otherwise this crude mixture is further nitrated to D.N.T.

2. *Dinitrotoluene.*—To the crude M.N.T. prepared in the manner described is added a stronger acid mixture, 670 kgrms. of 66° B. sulphuric acid, and 225 kgrms. of 46·8° B. nitric acid (specific gravity 1·445), over a period of six hours. In about 1·5 hours the temperature normally reaches 115° C. The operation is completed in a total time of nine hours, when the D.N.T. is separated hot from the acids and emptied into boiling water. If the course of the reaction has been defective, the oil ("Binitropfol") thus formed is allowed to drain off. Otherwise the total product is crushed and treated with water. Any impure product present collects on the surface of the water and can be removed. In Operations 1 and 2, 200 kgrms. of toluene yields 350–360 kgrms. of dry D.N.T., or 90–93 per cent of that required by theory.

3. By the use of still stronger acids the pure D.N.T. may be readily converted into T.N.T.

The methods of Häussermann, Vasquez, and Langscheidt are given in detail.

Description of Nitration Experiments. Four Methods of Preparing Trinitrotoluene.

The methods outlined above for the preparation of trinitrotoluene involve all of the four possible procedures for converting toluene into the desired product as follows:—

1. A one-stage method, comprising the direct nitration of toluene to trinitrotoluene in one operation.

2. A two-stage method, comprising—(a) the conversion of toluene into dinitrotoluene, and (b) the further nitration of the dinitrotoluene to trinitrotoluene.

3. A two-stage method, comprising—(a) the preparation of mononitrotoluene, and (b) the conversion of mononitrotoluene into trinitrotoluene.

4. A three-stage method, comprising—(a) the preparation of mononitrotoluene, (b) the conversion of mononitrotoluene, (c) the further nitration of dinitrotoluene to trinitrotoluene.

Method 1.—A modification of the method described by Vennin and Chesneau was employed by the author of this paper in the nitration of a laboratory sample of toluene boiling at 110·5° C. Because of the low yield of T.N.T.

(138 grms.—melting-point 79·5–81° C.—per 100 grms. of toluene), and the large amount of acid required, this method was abandoned as uneconomical.

Method 2.—No effort was made to utilise Method 2, on account of the recognised difficulties due to the formation of liquid products ("drip oil") along with the solid dinitrotoluenes. Two preliminary experiments gave very unsatisfactory results.

Methods 3 and 4.—Probably Method 4 is the one most commonly used by manufacturers of T.N.T., at least in this country, and in addition to any other economical advantages it may possess, it is much the most satisfactory if the manufacturer desires to utilise a part of the mononitrotoluene and dinitrotoluene products for purposes other than the preparation of T.N.T. But if it is desired to convert the toluene wholly into T.N.T. and no regard is had to intermediate products, except in so far as these affect the quality and amount of the final product, Method 3 seems to possess certain advantages. For the especial reason that Method 3 eliminates the necessity of separation of the D.N.T. mixture, the author selected it as most promising for investigation and development in connection with the nitration of the water-gas toluene. Method 4 was tried only by way of comparison with the procedure finally determined on the basis of Method 3.

Character of Toluene used in Experiments.

Results of Distillation.—A sample of the water-gas toluene (352·4 grms.), dried over calcium chloride for two days, was distilled from a 700 cc. flask provided with a Hempel still-head 26·7 cm. in length. The results of distillation were as follows:—

Results of Distillation of Water-gas Toluene.

Temperature interval, corrected, °C.	Weight of distillate, Grms.	Distillate, Per cent.
100–107·6	4·0	1·13
107·6–108·4	6·7	1·90
108·4–109·4	30·2	8·57
109·4–109·8	75·1	21·31
109·8–110·1	125·3	35·56
110·1	102·8	29·17
110·1	8·2 (a)	2·33 (a)
	352·3	99·97

(a) Remaining in still-head.

The boiling-point of pure toluene has been variously stated. Among the values given are the following:—Landolt and Jahn, 110° C. ("Molekularfraktion, &c.," *Zeit. Phys. Chem.*, 1892, Bd. x., 292); Timmermans, 110·7° C. $\pm$ 1 ("Sur la Purification et les Constantes Physiques de Quelques Liquides Organiques," *Bull. Soc. Chim. Belg.*, 1910, xxiv., 265); Neubeck, 110·8° C. ("Ueber Molekularvolumina Aromatischer Verbindungen," *Zeit. Phys. Chem.*, 1878, Bd. i., 656).

A sample of the toluene as received, not dried, was distilled in a similar manner. The first 10 per cent of distillate (up to 108·4° C.) came over milky, indicating the presence of water.

Determination of Specific Gravity.—The specific gravity of the toluene was determined with a pycnometer. Duplicate determinations of the specific gravity of a sample of the toluene which had been dried over calcium chloride gave the values 0·8658 and 0·8660 at 20°/4° C.

The specific gravity at 20°/4° C. of the fraction of the toluene distilling at 110·1° C. (102·8-grm. fraction mentioned under "Results of Distillation of Water-gas Toluene"), determined in the same manner, was 0·8657.

According to Landolt and Jahn, the specific gravity of pure toluene at 20°/4° C. is 0·86542. Calculated from their formula—

$$d \frac{t}{4} = 0·88418 - 0·00091961t$$

$$d \frac{20}{4} = 0·8658.$$

Freezing Tests.—A sample of the toluene after standing over calcium chloride for one week was cooled in a test-tube to -17°C . in an ice-salt cooling mixture. At this temperature there was a separation of a small quantity of white solid which when warmed again to -12°C . entirely disappeared. A sample of the fraction distilling at a temperature of $108.4-109.4^{\circ}\text{C}$. (see "Results of Distillation of Water-gas Toluene") behaved in the same manner. From the 110.1° distillate no such separation of solid occurred at -17°C .

One drop of pure benzene was added to a part of the 110.1° distillate. At -15°C . there was a separation of solid which melted again at -7°C . A drop of water added instead of the benzene to a part of the same distillate caused a separation of solid at -15°C ., which persisted up to $+5^{\circ}\text{C}$.

A sample of the original toluene dried over calcium chloride was cooled in a test-tube by means of a mixture of acetone and solid carbon dioxide. At -65°C . the total solid material separated was estimated as amounting to less than 1 per cent of the sample. This melted completely at about -12°C . There was no apparent increase of solid material separated at -77.5°C . At -79.5°C . less solid separated from the 110.1° fraction than from the dried toluene itself.

A sample of the dried toluene was cooled in a bath of gasoline cooled by means of liquid air. The whole solidified at -91°C . (uncorrected reading). It nearly all melted at -50°C . The freezing point of toluene as determined by Guttman is -92.4°C . ("The Determination of Melting-points at Low Temperatures," *Journ. Chem. Soc.*, 1905, lxxxvii., 1042). No identification of the approximately 1 per cent solid separating as low as -79.5°C . was attempted.

Dimethylsulphate and Sulphonation Tests for Paraffins.—The well-known dimethylsulphate and sulphonation tests for paraffins both gave negative results, but those tests were scarcely to be relied on in this connection.

The distillation experiments, specific gravity determinations, freezing tests, and dimethylsulphate and sulphonation tests indicated a high degree of purity for the toluene. The presence of some water and probably also of benzene was indicated. Whether other impurities were present and, if so, their nature was not established. However, the tests showed that the total impurities did not exceed approximately 1 per cent, and that figure was borne out by nitration experiments later described.

(To be continued).

STUDIES ON THE ORIGIN OF MISSOURI CHERTS AND ZINC ORES.*

By G. H. COX, REGINALD S. DEAN, and
V. H. GOTTSCHALK.

(Concluded from p. 68).

SPHALERITE.

Colouring Matter.

THE colouring matter of jasperoid having been determined to be due to colloidal sulphides, an investigation of that of sphalerite, which is colourless when pure, was undertaken. This study naturally divides itself into one of opaqueness and one of colour.

Opaqueness.

Opaqueness and colour, while here considered under the same heading, are not necessarily due to the same cause. While the opaqueness of the sphalerite of the Missouri and the Wisconsin fields is due largely to intense coloration, it is in part due to the presence of impurities, such as

chert fragments and a clay-like material, and to a great number of incipient fractures which, because of the high index of refraction of the blende, almost inhibit the penetration of light and even make microscopic study very difficult. Such fractions occur in surprising number, many of them being sub-microscopic in size. Indeed, so abundant are they that one is at first inclined to think that they have resulted from mining operations, yet so universal is their occurrence, even in crystals occurring in clay openings, that one is forced to conclude that they are either inherent in the crystal structure or have been formed by expansive forces created by the oxidation of included substances. If a drop of water is placed upon a sphalerite crystal which is apparently perfectly homogeneous and free from fractures, it will sink into the crystal in a short time. The same is true of galena crystals, of those of pyrite, and particularly so of those of marcasite. This fact was noted by Prof. Gottschalk, of the Chemistry Department of the Missouri School of Mines, in his work on the oxidation of sulphides, when he found that practically all of the sulphide ores seem to contain capillary openings such that when a crystal is heated in paraffin, bubbles rise from it for hours, indicating that air is being displaced. The ultra-microscope shows that sub-microscopic fractures are also present, as has been noted in the case of rock salt by Siedentopf (*loc. cit.*).

Colour.

Colloids.—It has long been recognised that the colour of sphalerite varies with its iron content, and that therefore it must be due to the presence of some iron mineral which, according to the common belief, is present as a solid solution with the sphalerite.

According to our present state of knowledge the colour of a solid solution bears an additive relation to the colours of its components. Zinc sulphide is white, ferrous sulphide is black, and a mixture of the two in the form of a solid solution should result in a grey, and not in the yellow, red, brown, and green colours so common in natural sphalerite. It is therefore not impossible that the colouring matter is largely iron sulphide and its alteration products, and that these occur mainly as ultra-microscopic particles forming a solid solution with the ZnS . Such a condition might readily produce the various colours observed, as in this case they would depend upon the degree of sub-division and not upon the colour of the particles.

In order to determine the presence or absence of colloidal particle pieces of sphalerite were examined by the use of the ultra-microscope. The method of investigation was practically the same as that outlined by Siedentopf Zsigmondy, and later by Siedentopf.

Much of the sphalerite was found to be so opaque that no light could be forced into it, but with clear pieces of sphalerite from Sonora, Mexico, and some semi-transparent and "ruby" blende from the Joplin district, good results were obtained. In all such cases a good light cone could be readily seen, proving the presence of colloidal substances.

(NOTE.—The source of the light is an ordinary arc lamp, the light from which is condensed by means of a lens having a 1 mm. focus, on a slit. The image of this slit is projected into the crystal, which is then examined by a microscope placed at right angles to the beam of light).

Liquid and Gas Inclusions.—If cleavage pieces with smooth surface were selected, a multitude of inclusions, mostly liquid and gas, could be seen with ease. While such inclusions were mostly sub-microscopic in size, some were sufficiently large to show negative crystals filled with liquid or gas, some showing a gas bubble in a liquid. Such liquid and gas inclusions seemed to be equally abundant in both the colourless and coloured sphalerite, and to show no relation to the intensity of colour. Some voids were large enough to be readily seen by the naked eye. A few measurable cubes of sulphides were also noted.

* Bulletin of the School of Mines and Metallurgy, University of Missouri.

The inclusions tend to follow possible cleavage directions, and in some cases minute fractures, but a large number of small particles may be found between such layers. This is what might be expected, since the inclusions in most minerals tend to follow such lines. Thus Siedentopf has shown that the ultra-microscopic particles which colour rock salt are largely grouped along such directions.

The number of these inclusions in the colourless Sonora sphalerite and the "ruby jack" of South-west Missouri, as shown by various observations, varying from a few thousand to some forty million per cm., the average being nearer the latter figure.

Solid Inclusions.—Smaller than the above and of a size probably about the limit of view of the instrument used, are believed to be the particles to which the main colour of sphalerite is due. These, because of their lack of movement, their abundance, the rough surfaces of the pieces used, the high index of refraction of the sphalerite, and the trouble experienced in narrowing the illuminating slit so as sufficiently to decrease the number of particles illuminated at one time, appear as a cloud rather than as individual particles. Their presence can hardly be doubted because of the illumination of the field of view, and the universal presence of the light cone, easily discernible in all translucent or transparent specimens. The size of these particles are therefore thought to be about the same or smaller than those of Zsigmondy's.

No. 3 gold solution (20 to 25 μ), which particles, although readily discernible in this instrument, probably would not be under the conditions of those in the sphalerite. The size of these particles is further evidenced by their colours, which correspond more nearly to those of gold solutions Nos. 3, 4, 5, and 6; i.e., those whose colours are due to particles between 20 and 150 μ .

Inasmuch as the colour of sphalerite varies with its iron content, and as iron disulphide is the only iron mineral that is commonly associated with sphalerite, it is natural to assume that the colouring matter is an iron compound and probably FeS_2 .

Examination has shown that nearly all specimens of sphalerite from the South-west Missouri and the Wisconsin zinc districts contain discernible crystals of FeS_2 , largely, if not entirely, as pyrite. Such included crystals vary in size from a quarter of an inch to those which can only be resolved by high power microscope. The smaller crystals are much the more abundant, and there is no reason to believe that this increase in number with a decrease in size does not continue in sizes beyond the limit of the microscope, sizes in which such crystals cannot be differentiated from inclusions of other substances.

We are thus led to conclude that the colour of this sphalerite is due almost entirely to the presence of iron sulphide (probably FeS_2 rather than FeS) and its alteration products. To this it may be objected that analyses of sphalerite high in iron from other districts do not show sufficient sulphur to make ZnS of the zinc and FeS_2 of the iron, and that therefore the iron must be present as FeS . It may be objected also that the specific gravity of sphalerite decreases with increasing iron, while it should increase if the iron is present as either FeS_2 or FeS as a colloidal solution, because the specific gravity of both of these compounds is greater than that of sphalerite. It is not clear that these objections are applicable to the Mississippi Valley ores, as the amount of iron is small, and the accurate determination of sulphur difficult and analyses lacking. And, while it is natural to assume that its presence in these ores is in the same manner as elsewhere, it is evident from the magnetism displayed by most of the western sphalerites that they contain iron in a form other than either FeS or FeS_2 , as will be shown later. It is also generally conceded that the zinc ores of the Mississippi Valley have had a different origin from those of the western states. Both of these apparent discrepancies may be in part, at least, explained by an alteration of the con-

tained iron sulphide, which would not only lower the sulphur content, but might also lower the specific gravity.

Oxidation of Sphalerite.—Microscopic examination indicates that very little of the sphalerite of the Missouri and Wisconsin fields retains its original colour, and that possibly most of the colour shown is due to alterations of substances originally contained as impurities within the sphalerite. This, if true, would mean that the original sphalerite was grey to green in colour and quite transparent in thin cleavage pieces, although here and there it contained very marked narrow bands of colouring matter. An alteration of the contained impurities, supposedly FeS_2 , would form the yellowish or straw-coloured varieties which are so common.

The irregular distribution of the yellow discolorations around nuclei of grey to green material usually bounded by possible cleavage directions apparently lead to no other conclusion. As surprising as this may seem, this is not at all incredible when one appreciates the great number of fractures contained in these crystals. Buckley and Buehler ("Missouri Bureau of Geology and Mines," vol. iv., 19, p. 54) noted the presence of surficial changes in sphalerite, concerning which they say:—"Wherever decomposition is taking place, the blende (in shale) faces are very black, the colour of the interior remaining unchanged." It is, however, our opinion that the oxidation of the contained iron sulphide has not been limited to surfaces of fractures, but that the oxidising substances, supposedly oxygen and water, have actually penetrated definite thicknesses of sphalerite. Roberts-Austen (*Phil. Trans. Roy. Soc.*, A, 1896, clxxxvii., 383) and later Van Ostrand and Dewey (*Prof. Paper No. 95*, G, U.S. Geol. Survey, 1915) have shown that gold will diffuse through lead with considerable readiness. In fact, the latter conclude that under certain conditions gold may diffuse into lead a distance of 25 inches in one hundred years. There is no apparent reason why oxygen and water may not diffuse through sphalerite.

The nearly colourless grey to green areas of unaltered sphalerite gave a good light cone in the ultra-microscope, thus showing that although the main colouring matter of sphalerite may now be due to secondary colloids, the primary substances also occurred in that manner. It should be noted that the differences in colour is believed to be due to difference in the size of the colloidal particles and not to their individual colour. Zsigmondy has prepared colloidal gold solutions ranging in colour from a nearly colourless light yellow (smallest size) through deeper yellows, through various shades of red, and from purple to green, and has shown that the colour depends entirely upon the size of the colloidal particles. Carey Lea has prepared colloidal silver solution of a great variety of colours (*Am. Journ. Sci.*, 1888, [3]). The fact that the green colloidal solutions are due to larger particles than those which are yellow or straw coloured, and that alteration products almost invariably occur in smaller pieces than the original substances, tend to confirm the above conclusions.

CONCLUSION.

When one considers that the jasperoid with which the South-west Missouri zinc ores are associated was carried and deposited in a colloidal form from the same solution as the sulphides, and that the colour of both the jasperoid and the sphalerite is apparently due to the presence of primary sulphides, and their alteration products which form a solid colloidal solution with them, it is but a step to the conclusion that these primary minerals were transported as colloids, or at least precipitated as such.

Recently a number of papers have been published calling attention to the possible application of colloidal chemistry to geologic processes, the net result of which seems to have been the confirmation of the results previously obtained by the chemists, namely, that sulphides can be carried in this manner. They have, however, all served to emphasise the fact that the application of colloidal chemistry to

geologic processes has not been critically considered, and that it is not at all impossible that the transportation of ore minerals as colloids may be of importance.

The finding of colloidal sulphides in ore and gangue minerals noted above is a step in advance, but in calling attention to the possible importance of sulphide colloids in the formation of ore deposits, and in particular to the South-western Missouri district, it is recognised that according to our present knowledge of the formation of colloidal solutions this could account only for the first concentration from a finely-divided source. Further investigation may show a method by which colloidal solutions may be formed in nature from other than finely-divided material, in which case this method might be applicable to some cases of secondary concentration.

The evidence in accord with the transfer of the metallic sulphides of the South-western Missouri zinc district as hydrosols is:—

1. The finely-divided state from which the deposits have been derived according to the present theories of origin.
2. The readiness with which hydrosols of PbS and ZnS can be formed.
3. The evident transportation and precipitation of these minerals with silica, which almost certainly has been carried as a colloid and precipitated by an electrolyte.
4. The presence of a suitable and abundant precipitating agent.
5. The presence of sulphide particles as original minerals, forming solid colloidal solutions with sphalerite and with jasperoid.
6. It provides a simple chemical explanation for the replacement of limestone and dolomite by sulphides, something which heretofore has been wanting.

THE SPECIFIC CONDUCTIVITY OF PURE WATER IN EQUILIBRIUM WITH ATMOSPHERIC CARBON DIOXIDE.*

By JAMES KENDALL.

1. Introduction.

The evaluation of the specific conductivity of pure water in equilibrium with the carbon dioxide of the atmosphere is a problem which is of especial importance in connection with the water correction in conductivity determinations. (This subject will be discussed fully in a forthcoming communication).

Carefully prepared conductivity water, when in contact with air, has been found by many observers to possess a constant specific conductivity of $0.7-0.8 \times 10^{-6}$ reciprocal ohms at the ordinary temperature (usually 18°). Considering the different methods of preparation employed by different investigators in different laboratories, the numerous values recorded in the literature are remarkably uniform. Whatever method may have been followed, and however small the specific conductivity of the water obtained may be when first prepared, its value rises rapidly on standing to the limits indicated above, and then remains practically constant.

The suggestion has frequently been made that the conducting impurity in such samples of water consists almost entirely of carbonic acid derived from the atmosphere. (See especially Kohlrausch and Holborn, "Leitvermögen der Electrolyte," p. 111, Leipzig, 1898; Walker and Cormack, *Journ. Chem. Soc.*, 1900, lxxvii., 5; Arrhenius, *Meddelanden fran K.-Vet. Akads. Nobelinstitut*, 1914, Band 2, No. 42). It is of interest therefore to test whether the directly-determined experimental value for the specific conductivity of water in contact with air is in agreement

with the value which may be calculated indirectly with the help of the following data:—

- (a) The ionisation constant of carbonic acid.
- (b) The mobility of the hydrogen carbonate ion, HCO_3^- .
- (c) The carbon dioxide content of the atmosphere.
- (d) The solubility of carbon dioxide in water.

Concordance between the observed and calculated values will obviously support strongly the validity of the above suggestion.

The figures at present available, however, for such a calculation are only approximate and incomplete. It is the purpose of this paper to establish exact values for all of the quantities tabulated above at 0° , 18° , and 25° —the three temperatures most generally employed in conductivity investigations. It may also be mentioned that an accurate knowledge of these quantities is of some importance apart from the present problem, since their use is essential in many geological studies and in questions of interest in various other fields. (For example, see R. C. Wells, *Journ. Wash. Acad. Sci.*, 1915, v., 617; Johnston, *Journ. Am. Chem. Soc.*, 1916, xxxviii., 947; Walker and Kay, *Journ. Soc. Chem. Ind.*, 1912, xxxi., 1013; Arrhenius, *Phil. Mag.*, 1896, xli., 237).

2. Previous Work.

The problem has already been taken up, for the temperature of 18° , in the researches of Knox (*Ann. der Phys.*, 1895, liv., 44), on the conductivity of carbonic acid solutions, and of Walker and Cormack (*Journ. Chem. Soc.*, 1900, lxxvii., 5), on the dissociation constants of very weak acids. (The figures given by Knox and in all succeeding references have, where necessary, been re-calculated from Siemens units to units of the reciprocal ohm).

The conductivity measurements of Knox, as will be shown in a later section of this paper, are obviously considerably in error; the method employed by him for the calculation of the solubility of carbon dioxide in water under atmospheric conditions is also inaccurate. Consequently, his conclusion that the calculated value for the specific conductivity of water in equilibrium with the carbon dioxide of the atmosphere (0.60×10^{-6} reciprocal ohms at 18°) is substantially identical with the direct experimental value of Kohlrausch and Heydweiller (0.64×10^{-6} reciprocal ohms at 18°) is not entirely convincing (*Zeit. Phys. Chem.*, 1894, xiv., 317).

The results obtained by Walker and Cormack are of much greater value. It was found that carefully purified Dundee water (prepared by three successive distillations, viz., from alkali, from phosphoric acid, and without the addition of any chemical) possessed a specific conductivity of 0.75×10^{-6} reciprocal ohms at 18° . The ionisation constant of carbonic acid at this temperature was found to be 3.04×10^{-7} (a value differing by 20 per cent from that obtained by Knox). The dilution of a solution saturated with carbon dioxide at a pressure of 760 mm. was taken as equal to 24 litres, according to Bunsen's absorption data. (These results may be in error by several per cent, as may be seen by reference to the original paper, *Ann.*, 1855, xciii., 1). Assuming the partial pressure of carbon dioxide in air to be 0.0003 atmospheres (obviously only a very rough approximation), the specific conductivity of water in equilibrium with atmospheric carbon dioxide was calculated to be 0.70×10^{-6} reciprocal ohms at 18° . The agreement of this value with that directly determined is clearly close enough to support the assumption that the specific conductivity of water in contact with air is to be ascribed almost entirely to dissolved carbon dioxide. Further confirmation was found in the results obtained from the application of a correction made under this assumption to the conductivity values of aqueous solutions of phenol (Walker and Cormack, *Journ. Chem. Soc.*, 1900, lxxvii., 18). This will be more fully discussed in a later communication.

It must be admitted, however, that the greater part of the data employed by Walker and Cormack in the above

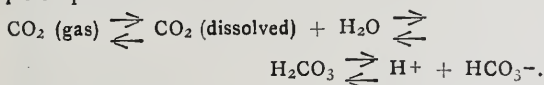
* From the *Journal of the American Chemical Society*, xxxviii., No. 8.

calculation is only approximate. In fact, the only exact figure utilised is that for the ionisation constant of carbonic acid, and even that differs considerably from the value found by Knox.

In the present paper, therefore, the conductivity measurements of Walker and Cormack for the temperature of 18° have been repeated, and results have also been obtained for two other temperatures—0° and 25°. Exact determinations have been made regarding the carbon dioxide content of the atmosphere, and more recent and accurate data for the solubility of carbon dioxide in water have been employed in the final calculations. The different steps necessary for the exact solution of the problem are taken up in the order below. The summarised results will be found in Section 8.

3. The Ionisation Constant of Carbonic Acid.

A solution of carbon dioxide in water possesses considerable electrical conductivity, due to the fact that the gas does not exist in solution merely as carbon dioxide, but also combines with the solvent to give the acid H_2CO_3 , which ionises into H^+ and HCO_3^- . The complete equilibrium to be considered is—



(The secondary dissociation of HCO_3^- into H^+ and CO_3^{2-} is so minute that it need not be taken into consideration here—McCoy, *Am. Chem. Journ.*, 1903, xxix., 437; Johnston, *Journ. Am. Chem. Soc.*, 1915, xxxvii., 2001).

The conductivity of carbonic acid solutions was first investigated by Pfeiffer at temperatures of 0° and 12.5° (Pfeiffer, *Ann. Phys.*, 1884, xxiii., 625). Ionisation constants were unknown quantities when these measurements were published, and since the results of Pfeiffer, recalculated according to the dissociation theory, have not previously been tabulated, they are summarised in the following table. The first column indicates the dilution of the solution in litres (V); the second the equivalent conductivity, Λ . (The determination of the equivalent conductivity at infinite dilution, Λ_∞ , which is necessary for the evaluation of k , is described in a following section); the third the dissociation constant k , multiplied by 107 to avoid an excess of zeros. Subsequent tables are arranged according to the same scheme.

TABLE I.—Carbonic Acid (Pfeiffer).

Temperature, 0°.			Temperature, 12.5°.		
V.	Λ .	$k \times 10^7$.	V.	Λ .	$k \times 10^7$.
2.37	0.167	1.68	2.79	0.304	3.18
3.07	0.188	1.65	3.29	0.334	3.25
3.85	0.213	1.69	5.27	0.421	3.23
4.39	0.235	1.81	6.59	0.450	(2.95)?
13.38	0.458	(2.26)?	13.38	0.661	3.14
∞	264.0	—	∞	323.0	—
Whence $k = 1.7 \times 10^{-7}$.			Whence $k = 3.2 \times 10^{-7}$.		

The constancy of the values in the last column is by no means all that could be desired at either temperature, and the dissociation constants given are, at best, only approximate values. This is probably due to the poor quality of water (specific conductivity = 3.2×10^{-6} reciprocal ohms) employed in the investigation; the conducting impurities present might suffice to account for a considerable portion of the measured conductivities.

The measurements of Knox (*loc. cit.*) may also be used to calculate the ionisation constant of carbonic acid at temperatures of 12.5° and 18°. Knox did not attempt to carry out these calculations himself; in an abstract (*Zeit. Phys. Chem.*, 1896, xvii., 186) an erroneous value is given, and Walker and Cormack (*Journ. Chem. Soc.*, 1900, lxxvii., 9) have given one series of results under the old Siemens units. The complete results of Knox have,

therefore, been calculated to modern units and are summarised in Table II.

TABLE II.—Carbonic Acid (Knox).

Temperature, 12.5°.			Temperature, 18°.		
V.	Λ .	$k \times 10^7$.	V.	Λ .	$k \times 10^7$.
10.48	0.603	3.32	12.61	0.778	3.76
12.24	0.652	3.32	14.54	0.838	3.79
15.43	0.735	3.34	24.9	1.090	3.75
20.79	0.853	3.36	53.2	1.581	3.70
29.77	1.019	3.35	125.0	2.445	3.77
∞	323.0	—	∞	354.0	—

Whence $k = 3.34 \times 10^{-7}$.

Whence $k = 3.75 \times 10^{-7}$.

The constancy of the values obtained by Knox appears to be quite satisfactory; the dissociation constant at 12.5° is also in good agreement with that given by the measurements of Pfeiffer. Nevertheless the later results of Walker and Cormack indicate that Knox's measurements also are considerably in error. The cause is again, most probably, the poor grade of water (specific conductivity as high as 2.8×10^{-6} reciprocal ohms) used in the determinations. Thus, at dilution 125 in Table II., the conductivity of the water amounted to 12 per cent of the total conductivity of the solution. For dilutions higher than 125, k is no longer a constant.

To be continued.)

CHEMISTRY AND PREPAREDNESS.*

LOOKING FORWARD TO TOMORROW'S NECESSITIES FOR INSURING COMFORT, PROTECTION, AND EVEN LIFE ITSELF, THROUGH THE EYES OF CHEMISTRY.

By HENRY P. TALBOT.

(Concluded from p. 72).

Nitrogen for Explosives.

IF we exempt potassium chlorate, there is no useful explosive which does not require nitric acid for its manufacture. As an index of the probable future needs, it is of interest to trace briefly the development of the modern explosives as used in the great war.

The useful explosives may be sub-divided into the propellants, employed in ballistics, and high explosives, used in blasting operations, and in torpedoes, mines, bombs, and shells. Only those substances can be successfully used as explosives which concentrate in a small space materials which will act upon each other with enormous rapidity, generating great volumes of gas, and liberating large quantities of heat, which, by expanding these gases, give rise to the propellant or rending force desired. Measured in our ordinary units of time all explosive action seems to be instantaneous, but accurate measurements show that there are real differences in the rate of decomposition, and it is exactly this which determines whether or not a given explosive can be used as a propellant. It is required of a perfect propellant that, "when fired in the breach of a gun, the combustion or decomposition shall commence comparatively slowly, gradually overcoming the inertia of the projectile without putting too great a strain on the gun itself, and then that the decomposition shall increase in rapidity, thus supplying gas more and more rapidly, accordingly increasing the momentum of the projectile, which should leave the muzzle of the gun with maximum velocity."

Within certain limits gunpowder is a satisfactory propellant, but smokeless powder is far more satisfactory.

Prof. Lewes, an English authority, furnishes some interesting comparisons. At the time of Napoleon's activities, the *Victory* was the most heavily-armed British

* Substance of a paper read before the Tuesday Club, of Newton, U.S.A., 1916.—From *Science Spectator*, vi., No. 4.

ship afloat. Her broadside of 52 guns, if fired simultaneously, would throw about 60 per cent of the weight of metal contained in one shot from a 15-inch gun of a superdreadnought. The 68-pounders of the Crimean war, using a charge of 16 pounds of black powder, are now replaced by the 15-inch guns, weighing 100 tons, from which a charge of 100 pounds of cordite (a smokeless powder) hurls a projectile weighing 1925 pounds with accuracy to a distance of fifteen miles, or, with high angle firing, to a much greater distance.

About 1850, the rifling of the bore of the guns was introduced, with a gain of range and accuracy, but requiring the lengthening of the barrel. At the siege of Alexandria in 1882, 80-ton guns, of 16-inch calibre, were used, while in 1886, 110-ton guns, with 16½-inch bore, requiring a charge of 960 pounds of powder, were employed.

It was found, however, that gunpowder was not a satisfactory propellant under the new conditions, since the velocity of gas generation decreased as the surface of the grains diminished in area, as they were consumed. Various expedients were tried, but none successfully. Moreover, the products of decomposition of gunpowder are about 50 per cent solids and remain as smoke, obscuring the vision of the gunner, and inviting attack from the enemy. A smokeless powder was evidently a necessity.

Schönbein, as far back as 1845, had prepared an explosive nitro-cotton, or nitro-cellulose, from cotton and nitric acid. It was natural to turn to this material. But it proved to be a high explosive rather than a propellant.

When cotton is treated with nitric acid, it is converted into nitro-cellulose, but it does not thereby lose its natural structure. Under the microscope the fibres of both cotton and gun-cotton are found to consist of very minute tubes, and if any of the gun-cotton begins to burn, the flames are forced by the high pressure into these tubes, and the whole mass decomposes so fast as to subject the guns to dangerous strains. It is as though one were to fan flames into a pile of straws; the inner and the outer surfaces would be exposed to the igniting effect of the flames.

Nitro-glycerin is an even more rapid explosive; and dynamite, which is nitro-glycerin absorbed in earthy material, while less dangerous to handle, is equally impossible as a propellant. It is of interest to recall in passing that Nobel, of peace-prize fame, was the inventor of dynamite.

In the course of time, it was found that if the nitro-cellulose is dissolved in acetone (an organic solvent derived from wood-distillation), and the acetone evaporated, the nitro-cellulose which is then recovered has lost its tubular structure, and then burns less violently. This was the basis of smokeless powder as late as 1838. It was far superior to gunpowder as a propellant, and yielded only gaseous products. Since then there have been innumerable patents issued for combinations of explosives under trade names. A typical case is that of cordite much used by the Allies, which consists of nitro-glycerin and nitro-cellulose, first dissolved together in acetone, with subsequent removal of the solvent. Under these conditions the nitro-glycerin goes to pieces more slowly than when used alone. Some vaseline is said to be added, which gives added stability and lubricates the gun. The material is cast into sticks, rods, or cords; hence the name.

The introduction of the smokeless powders caused an immediate change in gun construction, with a reduction of bore to 15 inches, and smaller firing chambers, since a charge of 400 pounds of cordite replaces the 600 pounds of prism powder, while a 50 per cent increase of velocity at the muzzle is attained, using a heavier projectile.

It is clear that the permanence during storage of these smokeless powders is a matter of first importance, and many combinations otherwise satisfactory have failed in

this respect. Many magazine explosions have been the result of spontaneous decomposition, accelerated by even slight amounts of decomposition products.

In contrast with the propellant, the successful high explosive must produce its maximum effect in the shortest possible time. These are used in the various forms of projectiles, mines, and torpedoes. The two last-named may be included with shells and bombs for our present discussion.

Shells are of two general classes: shrapnel utilised against troops in the field and high explosive shells intended to pierce armour-plate or reduce earth-works or wire entanglements. The shrapnel shell, as described by writers on the subject, is a hollow cylindrical steel projectile packed with bullets, at the base of which is a bursting charge that may be gunpowder or high explosive, while in the nose of the shell is arranged the time-fuse connected by a tube to the bursting charge, and so regulated that the shell can be exploded in the air at any desired point, the bullets and fragments of the shell being driven forward and spreading over a considerable area. The shrapnel used in the ordinary field-gun is an 18-pound projectile, containing 375 bullets, and when burst at the right altitude is a most deadly weapon against troops, especially when in massed formation.

The high-explosive shell is made of forged steel with comparatively thin walls and a heavy bursting charge, but the large naval shells and those for the siege guns, which have to penetrate heavy armour, are made from ingots of chrome or chrome-nickel steel, forged, hardened, and the nose capped with soft steel, which prevents the shell from shattering on impact with the hardened steel armour. These shells also contain a heavy charge of high explosive, generally cast into the shell in a fused condition.

Grenades are of the character of miniature shrapnel, but are filled with all sorts of fragments. The surgeons report finding among miscellany victrola needles within the internal economy of their patients. It is striking that, in the use of the grenade, there has been a return to the employment of the ancient catapult. The flight of the grenade through the air is steadied by a rod, if fired from a gun, or a rope tail if fired by hand.

The high-explosives employed in the various projectiles doubtless vary greatly. They include nitro-cellulose, and probably nitro-glycerin in admixtures. But we also find another type of explosive largely used, which is obtained by the action of nitric acid upon some of the coal-tar products. Two typical examples of such products are picric acid and trinitrotoluene, called T.N.T. The first of these is made from carboic acid (phenol) by a nitrating process. It is a yellow powder. Phenol occurs in coal-tar, but not in sufficient quantities to meet the present demand, and is made from benzene, another coal-tar product.

Picric acid itself can be melted and poured into the shells. It is *per se* a safe explosive, but it forms compounds with the metal containers which are very treacherous and very unstable. It also requires a powerful detonator, to ensure the high explosive effect, and this has led to some premature explosions of shells within the guns.

A somewhat less powerful explosive, but one which has not the disadvantages of picric acid, is the trinitrotoluene. The pressure produced by the former is 135,000 pounds per square inch, as compared with 119,000 for the latter. It does not attack the metal containers, and when mixed with other explosives produces such a shattering effect that the fragments of shell are larger and more destructive when in contact with earth works or wire. These shells on bursting emit an intense black smoke, which aids observers in determining the effectiveness of the gun-fire. The shells are known as "Jack Johnsons" or "Black Marias." The stunning and numbing effect on the men in the trenches is also said to be greater.

One of the most powerful explosives known appears to be a tetra-nitro-anilin, while a close relative, tetra-nitro-

methyl-anilin, known as "tetryl," is used as a primer or detonator.

Both picric acid and T.N.T. will burn quietly in the open, if ignited.

How, then, are they and other similar materials brought to explosion? In some cases by actual ignition. For example, the heavy charges of smokeless powder in the guns are usually ignited by means of a small charge of gunpowder placed in the chamber with the propellant, and this, in turn, is ignited by a detonator, which, as a rule, is a substance which is caused to decompose by shock. The so-called fulminate of mercury such as is used in ordinary cartridges, and exploded by the blow from the hammer of the weapon, is a material of this sort. When struck it explodes, either from the vibration of the blow or from heat generated by the blow. The explosion of the fulminate starts certain vibrations in the air or ether, and these seem to be of such a character as to be taken up by the molecules of the explosives, with the result that these, in turn, become disrupted. It is, in principle, like what occurs if a bow is drawn across the string of a violin in front of a piano when the loud pedal is pressed down. The single string of the piano which corresponds to the tone of the violin in its length of vibration will respond. It is also similar in principle to wireless telegraphy, save that in both these latter cases no decomposition of material ensues, while in the case of the explosive the molecules are shattered by the vibrations from the explosion of the fulminate.

The explosives all give out heat when they decompose, and heat, in turn, always hastens any chemical change. Hence, any decomposition caused by the vibrations of the detonator is at once propagated through the mass.

In the incendiary bombs, which are recently so much in evidence, they have found phosphorus, inflammable liquids of various sorts, and a mixture known and used in the arts, and called thermite. It consists of a mixture of oxide of iron and powdered aluminium. When ignited by a primer just before the bomb bursts, it generates an intense heat, and molten iron is scattered in all directions. This iron is, indeed, far above its melting point, attaining temperatures as high as 3000° C. Its incendiary capabilities are sufficiently evident. It is stated that phosphorus has also been incorporated in shrapnel and grenades. It aggravates the wounds produced, since the tissues burned by the phosphorus are only very slowly restored. It is also true that the phosphorus, which takes fire on exposure to the air, leaves a cloud of white smoke by day and a flash of fire by night, which again aids in locating the fall of the shell. They have been called the "woolly bears."

Of the raw materials demanded for these explosives, outside of nitrogen, we are fortunate with respect to cotton, iron, fuels, and metals, although there is an enormous demand for cotton. An adequate supply of glycerin calls for foresight. It is a by-product of the soap industry, and can be obtained from animal fats, and from some vegetable oils by other processes, but the ordinary sources of supply would probably have to be augmented to meet war requirements.

The poisonous gases employed in the present war appear to be chlorine, or mixtures of chlorine and some bromine. Both act violently upon the mucous lining of the throat and lungs, 2 per cent by volume of chlorine often proving fatal. Bromine is, if anything, even more poisonous than chlorine. It is a liquid at ordinary temperatures, and is supposed to be used in shells, since the liquid is scattered as such, and on evaporating does its cruel work. According to accounts, liquid chlorine, or more probably chlorine gas, has been forced through pipes in front of the trenches, and carried by the wind against the enemy. Only a heavy gas could be thus used. If chlorine is a fair weapon, we have a plentiful source of it in our salt deposits,

Liquid Fuel.

Both aircraft and undersea boats, in their remarkable development, have presented new problems which must be duly considered in a preparedness programme. From a chemical standpoint the most urgent of these are adequate supplies of liquid fuels, and the devising of metallurgical products which shall combine maximum strength with minimum weight. Much advance has been made in the production of alloys of aluminium and magnesium, the two available metals with the least specific gravity.

The liquid fuel problem is upon its face one of some seriousness. In this country gasoline may be said to be almost the only liquid fuel in use to drive the internal combustion engines. The use of these engines has increased with enormous rapidity, not only as motive power for vehicles and boats, but as stationary engines, and in the form of portable engines for farm use, concrete mixers, and the like. In the war area such motors are attached to almost every movable object from aircraft to ambulances, and even to field and siege guns. The heavy petroleum oils, from which the gasoline has been removed, are also used as fuels on some of our battleships, on some of the western railroads, and for boiler plants in localities in which such oil is readily obtainable at low cost.

Gasoline is not a chemical entity. It is a name for a mixture of volatile substances obtained by distillation from the crude natural petroleum. The supply of natural gasoline must ultimately depend upon the supply of these crude oils. Before the advent of the gas-motor, the oil refiners were at a loss to find a market for these volatile oils. The burning oils, kerosenes, were made to carry as much gasoline as the rigid legal requirements regarding fire-tests would permit. To-day the situation is reversed, and the gasoline at present on the market carries as much kerosene as the traffic will bear, that is, as much as can be used and still retain sufficient volatility to enable the vapour to pass with air from the carburettor to the cylinders of the engine in adequate quantity. Both carburettors and engines have been modified to meet this necessary change in the character of the fuel supply. Is the demand for such fuel actually outstripping the supply even upon a peace footing? The rapid rise in the price of gasoline would seem to indicate this, but an analysis of the situation leaves the matter somewhat in doubt, at least so far as the immediate future is concerned. The question is dealt with in detail in a communication dated February 2, 1916, sent to the U.S. Senate at its request by the Secretary of the Interior. The total production of crude oil in the United States in 1900 was 63 million barrels, in 1915 266 million; that of the world in 1900 was 149 million. In 1915 it had risen to 400 million. The consumption of gasoline in the United States in 1899 was about 7 million barrels, in 1915 it was 41½ million. The ratio of increase of production of crude oil is about 1 : 4½; the gasoline consumption 1 : 6. This result has been made possible by improved refinery methods, and by alterations in the character of the burning fluid known as gasoline, as just described.

In his response to the Senate inquiry as to the cause of the sudden rise in the retail price of gasoline, the Secretary names six contributing factors: (1) Increased consumption of gasoline, which was 25 per cent greater in 1915 than in 1914; (2) Increased exports (about 1½ million barrels in 1915); (3) Depletion of stocks of gasoline held in January, 1915. There is almost none so held to-day; (4) Decrease in the production of crude petroleum yielding the larger percentages of natural gasolines. In the "Cushing field" alone, the wells were, some months ago, yielding less petroleum than in April, 1915, by an amount equal to 50,000 barrels of gasoline a day; (5) Increase in price of crude petroleum, which has been advanced from 1.45 dols. per barrel on January 1, 1915, to 2.25 dols. per barrel on January 1, 1916. Gasoline has advanced from 12 cents to 21 cents (wholesale) in the same interval. - If

this advance in the price of the crude oil bears any relation to the ultimate natural supply, it must apparently be anticipatory to a large degree. The price of gasoline has advanced more than proportionately, but this may be partially accounted for by temporary inability of refiners to handle the necessary volume of crude material; (6) the last factor is what the Secretary calls "Financial influences," and under this caption he discusses the fluctuations of the stock quotations, and concludes that in the case of the larger and stronger companies the price which the consumer pays does not depend alone upon the cost of crude material.

Apparently, then, the current price of gasoline is not an accurate measure of the imminence of a dearth of liquid motor fuel.

Other figures of interest are also to be found in this letter. Experts have estimated that, taking into account the known possibilities, the various so-called "fields" of petroleum have been exhausted to amounts varying from 8 to 93 per cent. But they also estimate that these fields may yet be counted upon to yield something like seven billion six hundred million barrels of crude petroleum. There is no accurate factor by which to translate this into gasoline because of changing practices; perhaps it may represent two billion barrels. These figures also take no account of the oil-shales known to exist. These are rocks more or less saturated with petroleum. The total possible yield from shales of the same character as are now worked in Scotland might furnish further billions of gallons of crude petroleum.

So much for the natural gasolines. But our resources are by no means exhausted with them, although the situation demands careful and intelligent study, if we are to be in a position to meet emergency demands.

In the first place, we have means by which we can produce what may be called artificial gasolines. We are already condensing to a liquid, the natural gases which are associated with the petroleum deposits and mixing this very volatile material with kerosene, the mixture constituting an artificial fuel.

It has, moreover, been found that there are several ways in which the less volatile components of petroleum can be decomposed into substances which are readily volatile, and at least two commercial processes are now in operation to effect this conversion of heavy liquids into what is, in effect, a gasoline. These volatile substances are, in turn, used directly, or are mixed with some kerosene to make a burning fluid of acceptable quality. In this way the proportion of available material for gas-motors is much increased. It will be some time before such operations can be conducted on a 50,000-barrel-a-day scale, and we may probably expect to see the price of such fuel continue to advance in the immediate future if the principle of supply and demand is the controlling factor.

But gasolines are not the only type of liquid fuel which it is possible to use in motors. In Europe, benzol, a coal-tar product, has long been used, and it is reported that Germany is using at the present time a mixture of equal volumes of alcohol and benzol with much success. The production of benzol is essentially controlled by the market for coke. Alcohol can be produced in great quantities from potatoes, and also from sawdust and wood-waste. Both benzol and alcohol have the disadvantage that they are less volatile than gasoline, and require a "starter" of gasoline, but, with modifications of our present devices, particularly with respect to electric heaters, their use is practicable. In Germany they are said to be using gasoline to start the motor.

Obviously, the gas engine has proved its claim to permanence, and the importance of this form of motive power in peace or war can hardly be overestimated. If we have plenty of time to prepare, the liquid fuel problem may not be serious. In an emergency, it behoves our Government to be ready to meet an acute demand.

The lighter-than-air craft has not apparently appealed

to the Allies. If we should determine to add zeppelins to our outfit, hydrogen is to be had in plenty, by the electrolytic decomposition of water for initial inflation. To supply the constant loss through the envelope, an apparatus similar in principle to the acetylene generators formerly used on automobiles is now used, in which water can be dropped on a solid mixture such as silicon and caustic soda. Hydrogen gas is thus generated, and can be introduced into the envelope to compensate for losses. This apparatus is either carried on the dirigible or transported by automobile as needed.

Prognosis and Research.

These are but a few of the material demands which would confront us if our preparedness is ever to be tested. But back of these and vastly more important than any one of them is the need for something like an adequate notion on the part of our Government, and our industrial leaders who must actually supply our material needs of what research and scientific method stands for and can accomplish. However we may criticise Germany, we cannot avoid a tribute of respect to the thoroughness with which she not only anticipated the events and material conditions of the war, but has met the rapidly changing conditions with fresh and more efficient weapons and munitions. It is impossible to think of Germany as entering a war as we are said to have entered the Spanish war, with black powder, when all other nations, even Spain, were using smokeless powder. Nor can we think of Germany, or perhaps any other of the nations, with our resources and self-assumed responsibilities to our neighbours, continuing with but one single small plant (in North Carolina) equipped to fix the nitrogen from the atmosphere, without which it is hardly too much to say that we might be brought immediately to our knees in the event that the South American supply of nitrate was suddenly stopped by our enemies.

The well-worn expression "in times of peace prepare for war" can nowhere be better applied than in the encouragement of research. Our army and navy departments are not like our industrial concerns. The latter can afford to temporise and take chances on producing a profit from the use of antiquated machinery or methods. In the contest of war there is no quarter for weapon or craft that was the finest *yesterday*, and no time to wonder how the enemy manages to keep one lap ahead of us.

There is much evidence to show, in chemistry at least, that we can at least hold our own in the embodiment of chemical principles and laboratory processes in profit-producing large-scale plants, but we do need to cultivate a greater appreciation for the research spirit, which alone makes it possible to attack the new problems fundamentally: it represents the difference between office efficiency and manufacturing efficiency. We need far more of this spirit infused into the education of the selected body of youths in our colleges and we need to offer far more encouragement to research through added endowment. Meanwhile we must be thankful to Secretary Daniels for building possibly better than he knew when he proposed the Naval Consulting Board. Their proposal of five million dollars for research seems at first an excessive expenditure, but the single item of corrosion of boiler tubes involves a direct or indirect damage of 2,000,000 dols. a year to the navy, and a single private concern manufacturing automobiles finds it economical to spend a half million dollars a year in research and experimentation.

Some of the ablest men of the country are giving their best thought to the work of this Naval Board, and it deserves the support of all of us who are in a position to appreciate its deeper significance, including its influence upon all research in both pure and applied science throughout the country.*

(NOTE.—The Federal Government is now interesting itself actively in the nitrogen question and has secured the assistance of the National Academy of Science. The

Academy has also recently created a Research Council which is engaged in studying our natural resources with respect to men and opportunities for research, as well as the best methods for its encouragement and for the achievement of greatest productivity).

BRITISH MALAYA'S DEMAND FOR CHEMICALS.

THE demand for chemicals in British Malaya is increasing steadily, but as only the values are recorded in the official statistics it is difficult to say whether the increase is merely one of values and not of quantity. Probably the explanation is to be found in the enormously inflated price of acetic acid, used largely in the coagulation of latex on the rubber estates. For what they are worth, however, the following statistics will be found of interest:—

	Imports.	Exports.
1913	£42,827	£19,230
1914	79,122	21,919
1915	110,185	47,357
1916 (nine months) ..	264,242	38,115

It would appear from the records that the United Kingdom leads in this trade, but the war has interfered with the export of chemicals from England, and our ally Japan has not failed to benefit from the opportunity. Details are not yet available as to the countries of origin in 1916, but the following table is compiled from the official records for the previous three years:—

Imports into Straits Settlements.		1913.	1914.	1915.
From—				
United Kingdom		£23,789	£21,467	£27,679
Netherlands		15,615	18,211	20,670
Germany		9,101	4,156	144
Austria-Hungary		6,123	4,213	—
Belgium		5,020	4,109	—
Hongkong		4,439	6,672	8,184
Japan		1,861	8,978	27,461
British India		—	—	11,267
Java		—	—	3,677

Exports.		1913.	1914.	1915.
Malay States and British				
North Borneo		13,319	13,487	31,995
Netherlands India		3,798	6,104	10,979
Siam		1,277	1,498	2,195

From the above it will be observed that, in addition to Japan, British India, Hongkong, and Java, supplied the requirements unobtainable from Europe. Where the Hongkong supplies originated it is impossible to say, but, as that colony has no manufacturing resources of its own, the chemicals sent thence to the Straits Settlements may have come originally from the United States, or even Japan.

Anglo-Russian Commercial Connections.—Owing to the special importance, at the present time, of establishing commercial connections on a firm basis between the allied countries, with the object of ousting German intervention and competition, the Russo-British Chamber of Commerce at Petrograd takes this opportunity of requesting all British firms wishing to trade with Russia now or after the war, to send their catalogues and price-lists (not less than ten copies) to the Chamber. The catalogues in question will be placed in the special library of the Chamber, and will be distributed to Russian merchants interested in the development of their trade connections with England.—The Russo-British Chamber of Commerce, 4, Gorochovaia, Petrograd, Russia.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, January 25, 1917.

Sir J. J. THOMSON, O.M., President, in the Chair.

PAPERS were read as follows:—

"Spectroscopic Observations on the Active Modification of Nitrogen." (V.). By Hon. R. J. STRUTT, F.R.S.

1. The faint red bands 6394·45, 6468·53, 6544·81, and 6623·52 belonging to the first positive group truly belong to the afterglow spectrum of nitrogen.

2. The second positive group is entirely absent from the afterglow spectrum.

3. The β and γ group only appear when oxygen-containing gases are introduced into the afterglow, or are originally present in the nitrogen used.

4. Using nitrogen that only gives the β and γ bands very faintly, it is found that oxygen or nitric oxide added to the afterglow bring in the β and γ bands with a certain relative intensity which may be called the standard. Carbon dioxide gives greater relative intensity to the β bands, and carbon monoxide to the γ bands.

5. If nitric oxide or nitrogen peroxide is introduced in sufficient quantity into the overglow, the β and γ groups disappear and a visually greenish continuous spectrum, not extending into the ultra-violet, is substituted. Nothing like this is observed with the other oxygen-containing gases.

6. Nitric oxide in a blowpipe flame gives this same greenish continuous band, together with the γ but not the β group.

7. Chemical tests show that when oxygen is introduced into the afterglow there is no detectable oxidation of nitrogen, and certainly not nearly enough to account for the β and γ bands on the view that these are due to nitric oxide generated. No definite conclusion is reached as to the origin of the β and γ groups, except that they require the presence of both nitrogen and oxygen.

"Magnetic Induction and its Reversal in Spherical Iron Shells." By Prof. J. W. NICHOLSON and Prof. E. WILSON.

1. The paper contains a solution of certain problems which arise in the production of an effective magnetic shield for large spaces. These relate mainly to the effective demagnetisation of the shells of which the shield is constituted.

2. Theoretical solutions of problems relating to the effects of indefinitely closely wound coils on various shells of such a shield are given, and compared with the experimental values for an actual coil, as determined by an exploring coil and ballistic galvanometer.

3. The experiments supply an estimate of the deviations of Maxwell's formula, for the field inside a spherically wound helical wire, from the true values, when the spacing in the helix is of importance.

4. A study of the necessary interval between current reversals in the process of demagnetisation has been made, and it is shown that the delay in reversal of magnetic phenomena in considerable masses of iron, due to eddy currents, is negligible when the magnetic inductions are less than 300 C.G.S. units.

"The Two-dimensional Motion of a Plane Lamina in a Resisting Medium." By S. BRODETSKY.

The object of the paper is to discuss some of the types of motion of a plane lamina in a resisting medium, such as the air. Experimental laws of resistance are used for varying circumstances of shape and motion. The motion is in two dimensions.

Part I. deals with a lamina of large moment of inertia. For the case of no forces acting on the lamina other than the resistance of the medium, relations are obtained con-

necting the components of velocity, the rotation, and the time. The relations are exhibited by means of plotted curves from which the motion can be readily found. In the case of a wide lamina an investigation is given of the oscillatory part of the motion. The graphical method is then extended to the case where forces in addition to the resistance act on the lamina, notably gravity. The actual motion of a narrow lamina under gravity is plotted for various initial conditions. It is shown that ultimately the path oscillates about a line inclined to the downward vertical on the same side as the rotation.

In Part II, the case of a lamina whose moment of inertia is negligible is considered, and equations are found for correcting the paths found in Lanchester's phugoid theory, so as to make them more applicable to the actual motion of laminas.

Part III. treats of the oscillations about a steady fall. The vertical fall of a lamina is shown to be unstable unless the centre of mass is at a distance below the centre of figure lying between two limits given by a quadratic equation. The stability of a parachute with a hanging body attached to it is also considered.

Finally, photographs are reproduced verifying the motion found for a narrow lamina under gravity, and the varying degree of instability of the vertical fall with varying position of the centre of mass.

Ordinary Meeting, February 1, 1917.

Sir J. J. THOMSON, O.M., President, in the Chair.

Papers were read as follows:—

"Application of the Theory of Probabilities to the Study of *a priori* Pathometry." (Part II.). By Sir RONALD ROSS, K.C.B., F.R.S., and Miss H. P. HUDSON.

"Investigation into the Periodicity of Measles Epidemics in London from 1703 to the Present Day by the Method of the Periodogram." By JOHN BROWNEE, M.D.

"Causes Responsible for the Developmental Progress of the Mammary Glands in the Rabbit during the Latter Part of Pregnancy." By Capt. J. HAMMOND.

"Post-Estrous Changes occurring in the Generative Organs and Mammary Glands of the Non-pregnant Dog." By F. H. A. MARSHALL and E. T. HALLAN.

CORRESPONDENCE.

THE

INCORPORATED SOCIETY OF ADVERTISEMENT CONSULTANTS.

To the Editor of the Chemical News.

SIR,—The rumour that the Advertising, including the trade, Press is already scheduled as a non-essential trade under the National Service Scheme may be premature. It may not yet be too late to let the legislature and the public know how fatal to national prosperity, and, consequently, to the financing of the war, this would be.

A trade paper prospers strictly in proportion to its usefulness to the trade it serves. Its main support is from advertising, the readiest and most economical mode of communication between producer and distributor. Your readers are well aware of your value to themselves as a time-saver, an educator, and a business help. Now that so many commercial travellers are doing fine service in the King's forces, it would be an act of singular fatuity to deprive trade of the only thing by which the obstruction caused by the absence of travellers can be obviated, namely, the trade press.

By means of a paper like yours a message can be sent to a whole trade at far less than the cost of printing and

posting a circular, and at an insignificant decimal of the cost of sending travellers. You relieve the railways, the post office, and the printing and paper trades by your economical access to the distributors of merchandise. If you, and the representative organs of other trades, are to be closed down, it will be a sorry day for British trade, and for the war-chest.

My Council desires me to call your attention to this danger and invite you to speak out, while there is yet time.—I am, &c.,

THOMAS RUSSELL, President.

MISCELLANEOUS.

Royal Institution.—A General Meeting of the members of the Royal Institution was held on the 5th inst. The Duke of Northumberland, K.G., President, in the chair. E. Arthur Ashcroft, T. Radford Thomson, and Charles F. Cross were elected members.

Monazite and other Thorium Minerals in Ceylon.—The *Bulletin of the Imperial Institute* (vol. xiv., No. 3) contains a long and important report of recent work on monazite and other thorium minerals in Ceylon. The work, which was begun in 1903, was chiefly directed towards the discovery of fresh sources of supply of thorium containing minerals, and several promising deposits of monazite were found, especially in the shore sands of the south and south-west coasts. Some of the analyses showed about 48 per cent of monazite in the concentrates, and there should be no difficulty in preparing a high grade monazite concentrate from these residues.

Faraday Society.—A general discussion on "The Training and Work of the Chemical Engineer" will be held on Tuesday, March 6, 1917, at 8 p.m., in the rooms of the Chemical Society, Burlington House, W. Sir Robert Hadfield, F.R.S., President of the Society, will preside over the discussion, which will be opened by Sir George Beilby, F.R.S. Prof. F. G. Donnan, F.R.S., will read a paper on "The Training of the Chemical Student for Work in the Factory." Mr. Charles R. Darling will read a paper on "The Training of the Works Chemists in Physics." Mr. W. R. Cooper, M.A., B.Sc., will read a paper entitled, "A Plea for the Forgotten Factor in Chemical Training." The following have signified their intention of contributing to the discussion:—Mr. G. S. Albright; Dr. E. F. Armstrong; Dr. Charles Carpenter; Dr. Dugald Clerk, F.R.S.; Prof. E. G. Coker, F.R.S.; Mr. S. Z. de Ferranti; Mr. A. P. M. Fleming; Mr. E. Hatschek; Prof. G. G. Henderson; Prof. A. K. Huntington; Mr. H. A. Kent; Mr. W. McNab; Dr. R. Messel, F.R.S.; Sir Gerard Muntz, Bart.; Dr. F. M. Perkin; Mr. K. B. Quinan; Mr. W. Gathorne Young; and others.

MEETINGS FOR THE WEEK.

MONDAY, 19th.—Royal Society of Arts, 4.30. (Cantor Lecture). Town Planning and Civic Architecture, by Prof. Beresford Pite.

TUESDAY, 20th.—Royal Institution, 3. "Pain and its Nervous Basis," by Prof. C. S. Sherrington.

— Institution of Petroleum Technologists, 8. "Liquid Fuel and its Combustion," by J. S. Brame.

WEDNESDAY, 21st.—Royal Society of Arts, 4.30. "The Training of Educated Women for Secretarial and Commercial Work, and their Permanent Employment," by Mrs. C. Hoster.

THURSDAY, 22nd.—Royal Institution, 3. "Memorial Art in History," by Prof. E. S. Prior.

— Royal Society. "The Fossil Human Skull found at Talgai, Queensland," by S. A. Smith. "The Magnetic Storm of August 22, 1916," by Dr. C. Chree. "Ordinary Convergence of Restricted Fourier Series," by W. H. Young.

FRIDAY, 23rd.—Royal Institution, 5.30. "Some Guarantees of Liberty," by H. Wickham Steed.

SATURDAY, 24th.—Royal Institution, 3. "The Pronunciation of Languages in General," by D. Jones, M.A.

THE CHEMICAL NEWS

VOL. CXV., No. 2987.

THE SPECIFIC CONDUCTIVITY OF PURE WATER IN EQUILIBRIUM WITH ATMOSPHERIC CARBON DIOXIDE.*

By JAMES KENDALL.

(Continued from p. 79).

3. The Ionisation Constant of Carbonic Acid (continued).

THE careful measurements of Walker and Cormack at 18° are recalculated to modern units and given in Table III., below. A column indicating the ratio of the ionised to the total solute, $[a]$, is added.

TABLE III.—Carbonic Acid (Walker and Cormack), 18°.

V.	A.	a.	$k \times 10^7$.
27.5	1.033	0.00289	3.05
55.0	1.454	0.00407	3.03
82.5	1.784	0.00500	3.04
110.0	2.052	0.00575	3.02
∞	354.0	—	—

Whence $k = 3.04 \times 10^{-7}$.

The value of the ionisation constant is about 20 per cent less than the value calculated from Knox's figures, corresponding to an actual difference in the conductivity of 10 per cent. The better quality of the water used (specific conductivity = 0.75×10^{-6} reciprocal ohms) and the fact that a more exact method was employed for measuring the concentration of the solutions cause the investigators to conclude that their own numbers are probably the more accurate. ("A Modification of Pettenkofer's Method;" see Walker, *Journ. Chem. Soc.*, 1900, lxxviii., 1110).

This conclusion is confirmed by the present author's measurements, which are given in Table IV., below. The experimental method adopted for the conductivity determinations was precisely that followed and described in previous investigations (Kendall, *Journ. Chem. Soc.*, 1912, ci., 1275). A Cantor cell (with large electrodes only a small distance apart) was employed, this type possessing the advantage that successive dilutions can be made rapidly and accurately within the cell (Cantor, *Zeit. Elektrochem.*, 1903, vii., 922). A rotating commutator and a galvanometer were used in place of the more general induction coil and telephone, and gave satisfactory results throughout. The bridge employed was a three-meter platinum wire with one thousand divisions; readings could be obtained and duplicated to one-tenth of a division at all dilutions, the galvanometer being used as a zero instrument. The cells were immersed when in use in a large electrically-controlled thermostat, the greatest variations in temperature during the observation period being 0.005°.

The solutions of carbonic acid were prepared by passing pure carbon dioxide (obtained by the action of tartaric acid on sodium carbonate) first through several wash-bottles containing conductivity water, and finally through the water (60 cc. in volume) contained in the Cantor cell. (If the carbon dioxide is prepared by the action of hydrochloric acid on marble in the usual manner, a trace of hydrochloric acid is invariably carried over into the conductivity cell, in spite of the several intervening wash-bottles). The water employed possessed a specific conductivity of 0.60×10^{-6} reciprocal ohms at 0°, 0.75×10^{-6}

reciprocal ohms at 18°, and 0.85×10^{-6} reciprocal ohms at 25°. The method of its preparation will be described fully in a later paper.

The concentration of carbonic acid in each solution was determined immediately after the conductivity measurements had been completed, by running out half of the volume (30 cc.) from the cell and estimating its carbon dioxide content by a suitable modification of the Walker-Pettenkofer method. (The solution was run directly into a bottle containing air free from CO₂, excess of baryta solution of known concentration added, and the normal procedure then followed). The results obtained from duplicate experiments were in agreement within 0.2 per cent.

An examination of the last column of Table IV. will show that the ionisation constants obtained at each temperature are true constants throughout the whole range of dilutions. The value obtained at 0° is much higher than that given by the measurements of Pfeiffer; the value at 18° is in good agreement with that of Walker and Cormack.

TABLE IV.—Carbonic Acid (Kendall)

V.	A.	a.	$k \times 10^7$.
Temperature, 0°.			
25.4	0.631	0.00239	2.25
38.3	0.770	0.00292	2.23
50.0	0.888	0.00336	2.27
76.3	1.081	0.00409	2.21
99.8	1.242	0.00471	2.23
152.6	1.518	0.00586	2.27
∞	264.0	—	—

Whence $k = 2.24 \times 10^{-7}$.

[Temperature, 18°.

30.9	1.100	0.00311	3.13
42.0	1.281	0.00362	3.12
61.2	1.550	0.00438	3.14
83.4	1.792	0.00506	3.09
∞	354.0	—	—

Whence $k = 3.12 \times 10^{-7}$.

Temperature, 25°.

36.4	1.403	0.00357	3.51
51.3	1.659	0.00422	3.48
72.8	1.977	0.00503	3.49
102.4	2.341	0.00595	3.48
145.5	2.820	0.00717	3.55
∞	393.4	—	—

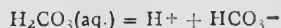
Whence $k = 3.50 \times 10^{-7}$.

4. The Heat of Ionisation of Carbonic Acid.

The accuracy of the values for the ionisation constant of carbonic acid given in Tables I. to IV. may be tested by calculating, from the figures for two different temperatures, the heat of ionisation, Q , according to the van't Hoff formula—

$$\log k_1 - \log k_2 = (Q/2.303 R) (1/T_1 - 1/T_2)$$

(where k_1 and k_2 are the dissociation constants at absolute temperatures T_1 and T_2 , respectively) and comparing the calculated value with that obtained by direct thermal measurements. The heat of the reaction—



is the heat of mixture of one mol. H_2CO_3 and one mol. NaOH, less the heat of neutralisation of one equivalent of a strong acid. From the measurements of Thomsen it is equal to —2800 cal. (Thomsen, "Thermochemische Untersuchungen," Leipzig, 1882).

The values for Q as calculated from the results tabulated above are given in Table V.

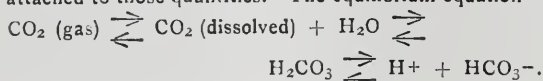
The agreement of the values of the present paper with that directly determined is very satisfactory, the results of Pfeiffer and of Knox, on the other hand, give figures which are far too high.

* From the *Journal of the American Chemical Society*, xxxviii., No. 8.

TABLE V.—Heat of Ionisation of Carbonic Acid.

Temperature interval.	Observer.	Heat of ionisation.
0—12.5°	Pfeiffer	—7850 cals.
12.5—18°	Knox	—3480 cals.
0—25°	Kendall	—2890 cals.
0—18°	Kendall	—2910 cals.
18—25°	Kendall	—2830 cals.

A careful consideration of the complete equilibrium in carbonic acid solutions, however, introduces a disconcerting factor into the above calculation. The "ionisation constants" and "heats of ionisation" given in the tables preceding have not the exact significance that is usually attached to those quantities. The equilibrium equation—



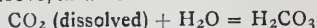
shows that the nonionised portion of the solute exists partly as H_2CO_3 and partly as CO_2 in the solution. The true ionisation constant—

$$(\text{conc. H}^+)/(\text{conc. HCO}_3^-)/(\text{conc. H}_2\text{CO}_3)$$

will therefore be different from (and greater in value than) that calculated in Tables I. to IV. according to the formula—

$$(\text{Conc. H}^+)/(\text{conc. HCO}_3^-)/(\text{conc. H}_2\text{CO}_3 + \text{conc. CO}_2).$$

Similarly the true heat of ionisation will differ from that calculated above, in which the heat of the reaction



is also included.

Owing to the fact that the ratio—

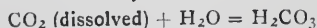
$$(\text{Conc. CO}_2)/(\text{conc. H}_2\text{CO}_3)$$

in the solution will not vary with the dilution (providing only dilute solutions are investigated (see *prox*), the "ionisation constants" obtained in the above tables still show a constant value, although they are not the true ionisation constants. The true values could be found from them if the ratio $(\text{conc. CO}_2)/(\text{conc. H}_2\text{CO}_3)$ at each temperature were known. Unfortunately there does not appear to be any simple way of evaluating this ratio; the conclusion of Walker and Cormack (*Journ. Chem. Soc.*, 1900, lxxvii., 13), recently re-expressed by Johnston, *Journ. Am. Chem. Soc.*, 1915, xxxvii., 2003) that it is less than unity at ordinary temperature, is quite devoid of experimental support (Walker, *Journ. Chem. Soc.*, 1903, lxxxiii., 182). In a following section, however, it will be shown that for the purpose of the present investigation the value of the ratio is quite immaterial, since it does not enter into any of the calculations involved.

Only with regard to the heat of ionisation does our lack of knowledge concerning the ratio—

$$(\text{Conc. CO}_2)/(\text{conc. H}_2\text{CO}_3)$$

cause any confusion here. For if the value of this ratio changes to any great extent within the temperature interval 0—25°, then the heat of hydration:—



must be considerable (either positive or negative according as the ratio increases or decreases). Heat produced (or absorbed) by this reaction is included in the "heat of ionisation" given by the measurements of Thomsen; consequently the true heat of ionisation may differ considerably from the value of 2800 cals. found by him. Any change in the ratio $(\text{conc. CO}_2)/(\text{conc. H}_2\text{CO}_3)$ within the temperature interval 0—25° also introduces considerable errors into the calculation of the (apparent) "heat of ionisation" by means of the van't Hoff equation, as given in Table V. Nevertheless, the fact that these calculated values show satisfactory agreement for different temperature intervals with the experimental value of Thomsen indicates that any disturbing factors are only small—i.e., that the heat of hydration is negligible and that the degree of hydration varies but slightly with temperature.

5. Velocity of the Hydrogen Carbonate Ion.

In order to obtain the values for Λ_∞ (the equivalent conductivity at infinite dilution) for carbonic acid given in Tables I. to IV. above, we require to know the velocities of the ions H^+ and HCO_3^- at the temperatures studied.

The velocity of the hydrogen ion at 25° has recently been determined by the present author (Kendall, *Journ. Chem. Soc.*, 1912, ci., 1275) and found to have the value 347.2 ± 0.4 . With the aid of the temperature coefficient given by Kohlrausch (*Zeit. Elektrochem.*, 1902, viii., 290) and the tables of Johnston (*Journ. Am. Chem. Soc.*, 1909, xxxi., 1010) the probable values for the remaining temperatures may be found: at 18°, 313.9; at 12.5°, 288; and at 0°, 239. The accuracy of these values naturally decreases as the extrapolation interval increases; the last value may be in error by 1 per cent.

The velocity of the hydrogen carbonate ion is not so accurately known. From conductivity measurements of sodium hydrogen carbonate solutions, Walker and Cormack (*loc. cit.*) deduced the value 40.4 at 18°. Since, however, the highest dilution investigated was 512 litres, the error of extrapolation to infinite dilution might be appreciable.

Conductivity measurements with more dilute solutions of both sodium and calcium bicarbonates at 25° have been described by the author (Kendall, *Phil. Mag.*, 1912, xxiii., 974) in a previous investigation. The values for HCO_3^- obtained from the two series were 46.0 and 46.5, respectively. These figures are rendered only approximate by reason of the grade of the conductivity water employed in the dilutions

(specific conductivity = 1.10×10^{-6} reciprocal ohms at 25°), which exercised a disturbing influence upon the values obtained at high dilutions and necessitated an uncertain correction. The measurements have therefore been repeated with a better sample of water, the experimental procedure (preparation of the solutions, estimation of their concentration, &c.) being exactly as described in the previous communication. The results are given in the following table:—

TABLE VI.—Sodium and Calcium Hydrogen Carbonates 25°.

NaHCO ₃ .		$\frac{1}{2}[\text{Ca}(\text{HCO}_3)_2]$.	
v.	Λ .	v.	Λ .
12.1	77.3	64	83.3
24.2	81.7	128	88.8
48.4	85.3	256	93.4
96.8	88.2	512	96.7
193.6	90.6	1024	99.6
387.2	92.4	2048	102.0
774.4	93.8	∞	107.7
1548.8	94.8		
3097.6	95.5		
∞	97.1		

The water employed in the dilutions possessed a specific conductivity of 0.80×10^{-6} reciprocal ohms at 25°. No correction has been made in the above values for the water conductivity. That this procedure leads to accurate values for bicarbonate solutions will be seen in a forthcoming paper, where it is also shown that the extent and influence of hydrolysis is inappreciable throughout the range of dilutions investigated.

The values for the equivalent conductivity at infinite dilution are derived by graphical extrapolation, according to the method of Bates (*Journ. Am. Chem. Soc.*, 1913, xxxv., 519). Subtracting the figures for the cation of each series ($\text{Na}^+ = 51.0$ and $\frac{1}{2}\text{Ca}^{2+} = 61.4$), we obtain the values 46.1 and 46.3, respectively, for the velocity of the hydrogen carbonate ion at 25°. The mean value, 46.2, identical with that previously determined, is employed for the calculation of the velocities for the remaining temperatures, an average temperature coefficient for the ion being assumed (Kohlrausch, *Zeit. Elektrochem.*, 1908,

xiv., 129). The results obtained are: at 18° , 40.1 ; at 12.5° , 35 ; and at 0° , 25 . The accuracy of these values is in each case commensurate with that given for the hydrogen ion at the same temperature.

The final values derived for the equivalent conductivity of carbonic acid at infinite dilution are therefore:

At 25° , 393.4 ; at 18° , 354.0 ; at 12.5° , 323 ; at 0° , 264 .

These are the figures which have been employed in Tables I. to IV.

The ionisation data for carbonic acid solutions having now been established, we require to know the concentration of that solution which is in equilibrium with the carbon dioxide of the atmosphere. For this purpose it is necessary to determine two quantities—the carbon dioxide content of the atmosphere and the solubility of carbon dioxide in water.

6. The Carbon Dioxide Content of the Atmosphere.

A general impression exists that the carbon dioxide content of the atmosphere is a quantity which, although always very small, varies widely according to the conditions. Among the factors that have been mentioned as producing variations are the following:—

(a) *Location*.—Land or sea, country or city, height above the ground, height above sea-level, altitude.

(b) *Time*.—Day or night, season of year, long-periodic changes.

(c) *Weather*.—Rain or fine, foggy or clear, sun or cloud, windy or calm, hot or cold.

(d) *Chance*.—Volcanic eruptions, forest fires, factory fumes, &c.

The actual effect of most of these influences is still uncertain. (Letts and Blake, *Proc. Roy. Soc. Dublin*, 1900, ix., 107, 436.)

If large variations do constantly occur, then obviously it will be impossible to calculate standard values for the specific conductivity of pure water in contact with air, since the concentration of the saturated solution will vary considerably with the conditions. Nevertheless the fact that the experimentally-obtained values of different investigators in different laboratories check so remarkably closely suggests that, even in a laboratory atmosphere, any variations are in general only of minor importance.

The question of the difference between a normal outdoor atmosphere and a laboratory atmosphere may first be considered. In this connection, the extensive researches of Benedict on the oxygen content of the atmosphere afford some interesting evidence ("The Composition of the Atmosphere," *Publ. Carnegie Inst. Wash.*, 1912). The normal carbon dioxide content of outdoor air was found by him to be 3.1 parts in 10,000 by volume (mean of 212 analyses). Even in the Grand Central subway station of New York City, during a rush hour, the value is only doubled—6.1 parts in 10,000. Observations on the air of a crowded business street in Boston showed only the slightest trace of an increase. Hence in a well-ventilated laboratory the divergence from the normal outdoor value should obviously not be excessive.

With regard to the influence of location, &c., the following quotation from a memoir by Letts and Blake (*loc. cit.*, p. 173) is, in view of the exhaustive nature of their tabulations, quite decisive: "It must be granted that the average amount of atmospheric carbonic anhydride is much the same under the most diverse conditions of weather, locality, season, &c. But, on the other hand, there can be no doubt that variations in the amount do occur. These variations, if small in actual amount, are relatively large, and correspond with fluctuations of at least 10 per cent of the total quantity."

The present author is fortunate in being able to give direct experimental results on this important part of the problem from four laboratories situated in widely-separated localities: Edinburgh, Petrograd, Stockholm, and New York City. The figures obtained are in entire agreement with the conclusions of Letts and Blake, the extreme

variation in any one laboratory being ± 5 per cent and for the whole range of observations being ± 10 per cent. Conditions were kept as nearly constant as possible by working in large well-ventilated rooms which contained no gas flames and were not employed for any other chemical work at the same time. The experimenter was the only person in the room and carefully abstained from smoking until determinations were completed.

Several methods were attempted for the estimation of carbon dioxide, but the only simple procedure to afford rapid and consistent results was the Walker modification of the Pettenkofer method (*Journ. Chem. Soc.*, 1900, lxxvii., 1110; see also Letts and Blake, *loc. cit.*, 219). This gave values for the carbon dioxide content of the atmosphere which, as checked by duplicate measurements and by blank experiments, were found to be accurate to less than 0.1 part in 10,000 of the total volume. For a description of the experimental procedure and for the method of calculating the results the original paper of Walker should be consulted.

The results obtained are summarised in Table VII. The values are expressed as parts of carbon dioxide in 10,000 parts by volume of air, without correction for moisture. They consequently represent partial pressures of carbon dioxide, in atmospheres multiplied by 10^{-4} .

TABLE VII.—Carbon Dioxide Content of the Atmosphere.

Number of determinations.	Carbon dioxide.		Vols. per 10,000.
	High.	Low.	
18	3.88	3.56	3.69 (a)
10	3.80	3.51	3.65 (b)
8	3.56	3.21	3.29 (c)
24	3.52	3.26	3.39 (d)
60	3.88	3.21	3.53

(a) University of Edinburgh, March, 1911.

(b) Technological Institute, Petrograd, January, 1913.

(c) Nobel Institute, near Stockholm, June, 1913.

(d) Columbia University, July, 1915.

From an inspection of the above figures it will be evident that the variations are within the limits indicated by Letts and Blake, the greatest divergence from the final mean value—out of a total of sixty determinations—being a little less than ± 10 per cent. If the results for any one laboratory only are considered, the maximum variation is in the region of ± 5 per cent.

Such fluctuations are, in fact, only what may be looked for under the circumstances. The experimental method is accurate to less than 0.1 part in 10,000 of the total volume, but this represents an error of ± 3 per cent in the carbon dioxide content. The tension of the water vapour in the atmosphere at the ordinary temperature of 20° may vary between 0 mm. and 17.5 mm., i.e., about 2 per cent of the total atmospheric pressure, and since the results in Table VII. are not corrected for moisture, this involves a corresponding variation of 2 per cent in the carbon dioxide content (in order that the values shown may represent actual partial pressures of carbon dioxide). The variations in the results for any one laboratory are thus practically accounted for. The larger variations in the mean value for different laboratories are in all probability due rather to small locality influences than to differences of ventilation. Thus the higher values at Edinburgh and Petrograd may be explained by the fact that the university buildings are situated in each instance near the centre of the city. The Nobel Institute, on the other hand, lies out in the country several miles from Stockholm, and the laboratories at Columbia are exposed to the fresh breezes across the Hudson even in July (also, at times, to the acid fumes from the new Jersey factories; when these were present in quantity, it was necessary to defer experimental work until the wind changed to another quarter).

As legitimately comparable values of another observer, the results of Letts and Blake for the carbon dioxide content of "air collected in a large unused room in Queen's College, Belfast, with open windows and free circulation" may be quoted (*loc. cit.*, p. 136). A total of twenty-three determinations shows the following values (expressed in parts per 10,000 by volume and not corrected for moisture): high, 3.73; low, 3.28; mean, 3.49; maximum variation ± 7 per cent.

It is evident, therefore, that the carbon dioxide content of the atmosphere of a well-ventilated laboratory, unused for other chemical work, is in all normal cases near to the average value of 3.53 parts in 10,000 by volume given in Table VII. above. The deviations may amount to ± 10 per cent. The fact may be pointed out at once, however, that such deviations will in no way vitiate the conclusions drawn in the following sections of this paper. A variation of 10 per cent in the partial pressure of carbon dioxide involves, indeed, a variation of only 5 per cent in the specific conductivity of the solution in equilibrium with the gas. (The specific conductivity varies as the square root of the partial pressure; see the following section). Variations of this magnitude are found in the observed values, as will be seen later.

In view of the relatively large errors that have been mentioned, it would be difficult to obtain a "standard value" for the carbon dioxide content of the atmosphere to a much higher degree of accuracy than the above, even if that content were (as it certainly is not) a true constant. The fact that exceedingly large variations (as much as 700 per cent) have been recorded by numerous observers is probably due to the faulty methods of estimation that have been generally employed. The most careful and recent analyses of pure out-door air indicate relatively constant values. Unfortunately most of the observations on record have been obtained in connection with non-chemical investigations, and these frequently betray the fact that at least a little knowledge of chemistry would have been of great assistance to the experimenter, both in the choice of a method and in the execution of the necessary manipulations.

(To be continued).

THE NITRATION OF TOLUENE.*

By E. J. HOFFMAN.

(Continued from p. 76).

Preparation of Mononitrotoluene.

THE first step in the nitration of toluene was performed in a simple apparatus of an ordinary wide-mouth bottle, of approximately 1-litre capacity, provided with a glass stirrer propelled by a small motor, and placed within a larger glass vessel through which water of the required temperature was allowed to flow. Temperature readings were made by means of an ordinary thermometer. The nitrating acid was placed in the bottle and toluene was introduced slowly, with constant stirring of the acid mixture, or the reverse procedure of adding the acid to the toluene was followed.

The details of two experiments designated "Procedure A" and "Procedure B" are given below as illustrating the method, and indicating the character and yield of the product.

Procedure A.—To 200 grms. of toluene cooled to 9°C . by ice water in the cooling vessel a mixture of 587 grms. of sulphuric acid of 1.84 specific gravity, and 293.5 grms. of nitric acid of 1.42 specific gravity (50 per cent in excess of theoretical nitric acid) was slowly added from a dropping funnel, with constant stirring of the contents of the bottle. The addition of the acid and the cooling of the reacting

mixture were so regulated that a temperature of $20\text{--}30^{\circ}\text{C}$. was maintained during the greater part of the operation. Owing to loss of control the temperature was as high as $30\text{--}50^{\circ}\text{C}$. for a few minutes in the early part of the operation. The time consumed in completing the introduction of the acid was one hour and twenty minutes. Afterwards the water in the cooling vessel was run out and stirring continued one half-hour longer. After standing over night in a separatory funnel the spent acid and the nitration product, a clear light-yellow liquid, were separated. The yield of crude M.N.T. as thus separated was 320 grms.

Eighty grms. of this crude product, corresponding to the yield from 50 grms. of toluene, was carefully washed with water till free from acid, dried over calcium chloride for several days, filtered, and weighed. The acid washings were made slightly alkaline with sodium hydroxide, and were extracted with ether. The ether solution dried over calcium chloride was used for extracting the M.N.T. adhering to the flask, and in the chloride used in drying the other larger fraction of the product. The total weight of M.N.T. thus obtained was 71.5 grms. This product had a specific gravity of 1.1818 at 22°C ., and a nitrogen content of 10.58 per cent. Pure M.N.T. contains 10.22 per cent nitrogen, and crude M.N.T., according to Escales, has a specific gravity of approximately 1.165. Fifty grms. of pure toluene yields theoretically 74.46 grms. of M.N.T.

For further nitration the crude unwashed product was used, so that no losses due to purification had to be considered.

Procedure B.—In the second experiment the same weights of toluene and acids were used as in the first, but the toluene was added to the acids. Otherwise the procedure was the same. Little difficulty was experienced in maintaining a temperature of $13\text{--}30^{\circ}\text{C}$. during the operation of mixing, which lasted two hours. As before, the stirring was continued one half hour after the mixing had been completed. The yield of crude product was 331.4 grms. Purified as above, 248.55 grms. yielded 243.4 grms., having a specific gravity of 1.2450 and a nitrogen content of 12.14 per cent.

The high values for specific gravity and nitrogen were due to the formation of considerable dinitrotoluene, as the following data regarding the product show:—

Results of Distillation of 111.8 grms. of Crude Mononitrotoluene at a Pressure of 30 mm.

Fraction.	Temperature interval ($^{\circ}\text{C}$.).	Weight of fraction (grms.).	Fraction (per cent).
A	115—160	68.1	60.91
B	162—185	40.7	36.41
Residue ..		2.5	2.68
Loss		0.5	

Fraction A was a liquid having a specific gravity of 1.1750 and a nitrogen content of 10.34 per cent, or practically pure M.N.T., which contains 10.22 per cent nitrogen.

Fraction B was a white solid mass containing 15.13 per cent nitrogen, or nearly pure D.N.T., which contains 15.38 per cent nitrogen.

Calculated from the data of the nitrogen determination of the purified products before distillation, the values of 62.93 per cent and 37.07 per cent are obtained for the mononitrotoluene and dinitrotoluene contents respectively, which are in close accord with the distillation values. These calculations are necessarily based on the assumption that only M.N.T. and D.N.T. were present.

A further simple calculation is as follows:—100 grms. of toluene yielded 162.26 grms. of purified product, or 102.11 grms. of M.N.T. (62.93 per cent) and 60.15 grms. of D.N.T. (37.07 per cent). The latter quantity of D.N.T. corresponds to 45.28 grms. M.N.T. Hence the 100 grms. of toluene yielded a total of 147.39 grms. of M.N.T., which in turn corresponds to 98.98 grms. of toluene.

* From a technical paper issued by the U. S. Bureau of Mines. From *Chemical Engineer and Manufacturer*, xxiv., No. 5.

In view of the above results it is evident that Procedure B cannot be followed if the non-formation of dinitrotoluene is desired. In that case, of the two procedures, Procedure A must be followed instead. Other experiments indicated, however, that Procedure B may be used with little formation of D.N.T., provided the excess of nitric acid over the theoretical amount required for the nitration is small. But under such conditions some of the toluene will escape nitration; the product obtained in one experiment in which an excess of 25 per cent nitric acid was employed had a strong odour of toluene. In the use of less than 40—50 per cent excess nitric acid in Procedure B, the further difficulty of maintaining the progress of the reaction and also of avoiding the formation of very dark reaction mixtures, often of dark sludge, resulting frequently in the impossibility of separating the product from the spent acid, is to be ascribed to the depletion of the nitric acid by the formation of D.N.T. With 50 per cent excess nitric acid, however, no such difficulty was experienced, and if the temperature of reaction was not allowed to exceed 50° C. the resultant product was a clear yellow liquid from which the spent acid was readily drawn. If, on the other hand, a greater excess of nitric acid than 50 per cent is employed for nitration the proportion of D.N.T. formed may be large enough to result in its separation from solution in the liquid M.N.T., with consequent difficulty in effecting a separation of the product from the spent acid, and in the possible difficulties encountered when T.N.T. is prepared from D.N.T. In one experiment 50 grms. of toluene treated with an acid mixture containing 100 per cent excess nitric acid yielded 90 grms. of a crude product which was almost entirely solid D.N.T.

Inasmuch as the resultant crude product designated as M.N.T. is to be used for the preparation of T.N.T., the formation of D.N.T. is of much less consequence than is the loss of toluene, and besides some 40 per cent of the 50 per cent excess nitric acid is used up in converting a part of the M.N.T. into D.N.T. For these reasons and because the temperature of nitration was easier to control than in Procedure A, Procedure B was followed in the preparation of M.N.T. in most of the experiments. In general, effort was made to keep the temperature of reaction below 30° C., and no subsequent heating was required. But the experiments did not show that a temperature as high as 50° C. either decreased the yield or affected seriously the character of the product.

Table 1. gives data regarding the experiments upon which the above conclusions are based.

Preparation of Trinitrotoluene from Mononitrotoluene.

The preparation of trinitrotoluene from the crude mononitrotoluene was accomplished in an apparatus similar to that used in the preparation of the M.N.T. The vessel in which the nitration was effected was a tall beaker without lip, which was 23 cm. high and had a diameter of 8 cm. The beaker was placed on a sand bath which could be heated with a gas-burner as desired. To serve as a cover for the beaker a Florence flask from which the bottom had been removed, and to which a second neck about 1 cm. in diameter had been sealed at a distance of about 3 cm. from the original neck and parallel to it, was placed so as to fit closely on the flange of the beaker, the necks extending downward for about 6 cm. into the beaker. Through the smaller neck a thermometer was inserted; the larger neck equidistant from the sides of the beaker carried the glass stirrer and served as the opening through which the acids were dropped from a separatory funnel. The temperature of nitration was controlled by varying the rate at which the nitrating acid was added, and by raising or lowering the flame.

At the completion of each operation the reaction products were allowed to cool to about 100° C., when they were transferred to a specially constructed separatory funnel by means of which a hot separation of the liquid nitration product was made; or, as was the general procedure, the

contents of the funnel were allowed to stand about eighteen hours, during which time the supernatant liquid T.N.T. would solidify as a hard cake and the dissolved T.N.T. would crystallise out beneath. The spent acid was drained off from below. The solid cake of T.N.T. from either procedure was crushed, combined with the remainder of the solid separated, and washed well with cold water. Afterwards this was repeatedly washed in the molten condition with hot water until free from acid. When the spent acids were poured into approximately 5 to 10 volumes of ice-water and ice a second lot of crude T.N.T. was obtained and treated in the same way. The crude products were then dried either over sulphuric acid in a vacuum desiccator or in an electric oven at a temperature of 50—60° C.

If further purification of the crude T.N.T. thus obtained was desired, this was accomplished by crystallisation from a mixture of 9 parts of 95 per cent alcohol and 1 part of benzene, or by the simpler operation of shaking the finely powdered solid for a short time with a cold mixture of the composition mentioned.

Four Series of Experiments.

Four series of experiments covering the preparation of T.N.T. from M.N.T. were performed as outlined below.

Series 1.—In Series 1 the mononitrotoluene was dissolved in 100 per cent sulphuric acid, and nitrated with a mixture of equal parts by weight of nitric acid of specific gravity 1.5, and of 100 per cent sulphuric acid. The M.N.T. used in each experiment was the total product obtained from the previous treatment of 50 grms. of toluene. As 50 grms. of pure toluene yields theoretically 74.46 grms. of M.N.T. the latter figure was assumed to be the weight of the M.N.T. in the crude product in calculating the amounts of nitric acid to be used in each experiment. To convert 74.46 grms. of M.N.T. into T.N.T. requires theoretically 64.48 grms. of anhydrous nitric acid, or 72.78 grms. of 94.09 per cent nitric acid having a specific gravity of 1.5.

Series 2.—In the experiments of Series 2, with the exceptions noted, the mononitrotoluene was dissolved in sulphuric acid having a specific gravity of 1.84, and was nitrated with a mixture of equal parts by weight of nitric acid having a specific gravity of 1.5 and of 100 per cent sulphuric acid.

Series 3.—In the experiments of Series 3 the nitration of M.N.T. may be considered as having been performed in two stages, but without a separation of the dinitrotoluene formed in the first stage of the nitration.

Except in one experiment the M.N.T. dissolved in sulphuric acid of specific gravity 1.84 was first treated with a mixture of equal parts by weight of nitric acid of specific gravity 1.5, and of sulphuric acid of specific gravity 1.84.

At the end of this stage in the nitration 15 per cent oleum was added to the reaction mixture to concentrate the acids, after which the nitration was completed with a mixture of equal parts by weight of nitric acid of specific gravity 1.5 and 15 per cent oleum.

Series 4.—In the experiments of Series 4 trinitrotoluene was prepared from mononitrotoluene in two distinct steps involving the actual separation of the D.N.T. formed in the first stage of nitration. The experiments were made for the purpose of comparing the results with those of the experiments in Series 3.

Summary.

The results obtained in the experiments herein reported, especially those in Experiments 4 and 5 of Series 3, lead to the conclusion that the following procedure will give the best results in the preparation of trinitrotoluene.

Outline of most Favourable Method of Preparing Trinitrotoluene.

The acid used in the first stage of the nitration of the toluene should be a mixture of two parts by weight of sulphuric acid of specific gravity 1.84, and one part of nitric

TABLE I.—Data regarding Experiments covering Preparation of Mononitrotoluene from Toluene.

Experiment No.	Weight of toluene (grms.).	Per cent of nitric acid in excess of theoretical.	Ratio of nitric acid to sulphuric acid.	Temperature of mixing (°C.).	Time of mixing (minutes).	Subsequent heating (°C.).	Yield of crude M.N.T. (grms.).	Yield of acid-free and dry M.N.T. (grms.).	Specific gravity of acid-free and dry M.N.T.	Per cent of nitrogen.
1.	50	10	1:2	20-30	30	One and a-half hours at 90-95°	72	—	—	— (e)
2.	50	10	1:3	25-35	35	One hour up to 95°; two hours at 95-97°	—	—	—	—
3.	50	25	1:3	20-30	25	None	74.0	67.3	—	— (f)
4.	50	25	1:3	25-55	20	Two hours up to 94° (a)	—	—	—	— (g)
5.	50	40	1:2	25-50	25	None	79.0	75.7	1.2194	11.17
6.	50	50	1:1.5	20-30	25	One hour up to 70°; one hour at 70-85°; three hours at 85-90°	81.0	—	—	—
7.	50	50	1:1.5	20-30	40	A few minutes at 50°	81.0	—	—	—
8.	50	50	1:2	25-30	40	Two hours up to 97°; two hours at 93-97°	82.0	—	—	—
9.	50	50	1:2	25-30	25	None	82.0	78.0	—	11.36
10.	50	50	1:2	25-55	25	None	81.0	78.2	1.2400	—
11.	50	100	1:2	20-30	40	Four and a-half hours at 90-95°	90.0	—	—	— (h)
12.	50	50	1:2	25-30	45	Half hour up to 95°; half hour at 95-97°	81.8	—	—	—
13.	100	50	1:2	22-49	35	None	165.1	—	—	—
14.	100	50	1:2	25-58	18		164.0	—	—	—
15.	100	50	1:2	25-50	53		163.0	—	—	—
16.	200	50	1:2	12-30	105		328.4	—	—	—
17.	200	50	1:2	15-36	110		328.0	(b) 73.0	—	—
18.	200	50	1:2	9-30	80	None	320.0	(c) 71.5	1.1818	10.58 (i)
19.	200	50	1:2	13-30	120		331.4 (d)	243.4	1.2450	12.14

(a) Excess HNO₃ increased to 50 per cent.

(b) From 82 grms. of crude product.

(c) From 80 grms. of crude product.

(d) From 248.55 grms. of crude product.

(e) Dark green mixture; no separation.

(f) Dark red product; odour of toluene.

(g) Black mixture; no separation.

(h) Product mainly solid dinitrotoluene.

(i) Acid added to toluene.

acid of specific gravity 1.42, the weight of nitric acid taken being 50 per cent in excess of that required theoretically for the conversion of all the toluene into mononitrotoluene. For 50 grms. of toluene 73.38 grms. of nitric acid is used.

To the mixed acid contained in the nitrating vessel provided with apparatus for cooling and stirring, and cooled to 20° C. or lower, the toluene is added gradually, with constant stirring, the rate of introducing the toluene and the cooling of the reaction mixture being so regulated that the temperature does not exceed 30° C. When approximately 70 per cent of the toluene has been added the nitration becomes much slower and little cooling of the mixture is required. When the total amount of the toluene has been introduced and the temperature ceases to rise, the cold water surrounding the nitrating vessel is allowed to run out while the operation is continued about one-half hour longer. After the contents of the nitrating vessel has stood for some time, preferably over night, the spent acids are removed by gravity from the supernatant crude mononitrotoluene, which consists of a mixture of mononitrotoluenes and dinitrotoluenes.

Preparation of Trinitrotoluene from Mononitrotoluene.

First Stage.—The mixed acid used in the first step in the conversion of the crude mononitrotoluene into trinitrotoluene consists of equal weights of sulphuric acid of specific gravity 1.84 and of nitric acid of specific gravity 1.5, the nitric acid content being 50 per cent in excess of that required theoretically to convert the calculated yield of mononitrotoluene into dinitrotoluene. For the product derived from 50 grms. of toluene, 54.58 grms. of nitric acid is taken.

The crude mononitrotoluene is dissolved in sulphuric acid having a specific gravity of 1.84, the weight of the acid being equal to the weight of mixed acid, and is heated to 50° C. The mixed acid is added gradually, with constant stirring, over a period of at least one hour, during which time the temperature should not exceed 100° C.

After all the acid has been introduced the mixture is heated for two hours at a temperature of 90-100° C.

Second Stage.—At this point the acids in the nitrating vessel, cooled to about 90° C., are concentrated by the addition of 15 per cent oleum, equal in weight to the weight of the mixed acid to be used in completing the nitration. If the oleum is added slowly little rise in temperature occurs.

The mixed acid used consists of equal weights of nitric acid (specific gravity, 1.5) and 15 per cent oleum, the nitric acid taken being double that required theoretically to convert into trinitrotoluene the nitration products calculated as dinitrotoluene. On the basis of 50 grms. of toluene, 72.78 grms. of nitric acid is used.

The mixed acid is added gradually with continued stirring, while the temperature is allowed to rise up to, but not above, 115° C. When approximately 75 per cent of the acid has been introduced heating is required to maintain the temperature above 100° C. A minimum time of two hours should be allowed for the introduction of the acid. When the addition of acid has been completed the heating is continued for two hours longer, a temperature of 90-117° C. being maintained, but the latter temperature should not be exceeded.

Upon the completion of the nitration the reaction mixture is allowed to cool in a vessel adapted to the subsequent removal of the spent acid. After standing at least eighteen hours the crude trinitrotoluene will have separated as a solid cake and suspended crystals. After the underlying spent acid has been drained off the crude product is crushed, washed well with cold and hot water, dried, &c., as previously described. A higher degree of purity may be obtained by washing with the alcohol-benzene mixture.

The spent acid contains in solution additional trinitrotoluene as well as lower nitration products, which may be recovered by precipitation in water. In practice the spent acid is used over again after renewal by the addition of fresh acids.

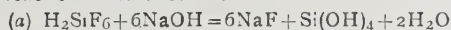
A STUDY OF THE SEPARATION OF HYDROFLUORIC ACID AND FLUOSILICIC ACID.*

By J. G. DINWIDDIE.

THE work to be described in this article was done with a view towards finding some satisfactory method for the analysis of a solution containing both hydrofluoric and fluosilicic acid.

The importance of an accurate method for this determination lies in the fact that commercial hydrofluoric acid very often contains as an impurity fluosilicic acid, which is of no use in etching, and which is a nuisance in analytical work. The value of a solution of hydrofluoric acid is obtained often by direct titration with alkali using phenolphthalein as indicator. Under these conditions each molecule of fluosilicic acid, H_2SiF_6 , requires six molecules of alkali for neutralisation, and therefore will be counted as six molecules of hydrofluoric acid.

Almost the only attempt to discriminate between these two acids when present together has been made by Katz (*Chem. Zeit.*, 1904, xxviii., 356), who titrates first in water solution and then in alcoholic solution together with potassium chloride in order to get a differential equation. The reaction in water solution is—



and in 50 per cent alcoholic-potassium-chloride solution,—



The hydrofluoric acid requires the same quantity of alkali for neutralisation whether titrated in water or in alcohol solution, while the fluosilicic acid requires one-third of the alkali in alcoholic-potassium-chloride solution that it does in water solution.

Were there no complications in the above reactions, the calculation of the results would be as follows:—

Let x be the volume of alkali required for neutralising the hydrofluoric acid, and let y be that required by the fluosilicic acid in the alcoholic solution. Then $3y$ will be required by the fluosilicic acid in water solution.

Then,—

$$x + 3y = \text{cc. req. in water titration} = a$$

$$x + y = \text{cc. req. in alcohol titration} = b$$

$$\therefore 2y = (a - b)$$

Thus the difference between the amount of alkali required for the water and for the alcohol titration is equivalent to two-thirds the amount which would be required for the fluosilicic acid alone in water solution.

In testing this method on a mixture of known concentration, Katz finds that the alcoholic-potassium-chloride titration requires considerably less than the theoretical amount of alkali. He explains this result by assuming that some of the free hydrofluoric acid is absorbed by the precipitated potassium fluosilicate, and is thus kept from being neutralised. Using normal and twice normal alkali for titrations, he gets results which tend to indicate that for very small amounts of fluosilicic acid, each molecule carries down with it one molecule of hydrofluoric acid, while for larger amounts three molecules carry down two of hydrofluoric acid.

On this basis he makes out a sliding factor to be used according to the relative proportions of the two acids present. For the fluosilicic acid content, if the difference between the water and the alcoholic titration is—

5 per cent or less of the water titration, multiply it by (0.0576);

5 to 10 per cent of the water titration, multiply it by (0.058—0.0595);

10 to 12 per cent of the water titration, multiply it by (0.06—0.061);

Over 12 per cent of the water titration, multiply it by (0.0617).

These factors are calculated on the basis of $\frac{2}{N}$ alkali.

Since Katz uses twice-normal alkali, and uses only from 3 to 8 cc. in a number of the titrations, there is ample room for very large percentage errors.

Before attempting to go farther, it is thought advisable to repeat some of Katz's work as well as to compare the titration of pure fluosilicic acid in water and in alcoholic potassium-chloride solution.

For a comparison of the two titrations of the pure acid, three samples were used:—No. 1 was made by suitable dilution of Baker and Adamson's commercial fluosilicic acid; Nos. 2 and 3 were made by treating silica and calcium fluoride with concentrated sulphuric acid, passing the evolved silicon tetrafluoride through a double coil of glass tube (water cooled), and then into water where the fluoride of silicon was decomposed into fluosilicic acid and silica.

Table I. shows the results of these titrations.

TABLE I.

(Alkali used was approx. 0.33 normal NaOH).

	H_2SiF_6 grm. of solution.	NaOH req. (in alcohol). Cc.	NaOH req. (in water). Cc.	NaOH req. (cc. per grm.).
No. 1	7.6774	—	42.1	5.48
	6.6227	—	36.3	5.481
	8.5302	15.9	—	1.864
	8.4770	15.7	—	1.852
Cc. of solution.				
No. 2	10	—	35.78	—
	10	—	35.79	—
	10	—	35.80	—
	10	—	35.80	—
	10	12.27	—	—
	10	12.30	—	—
No. 3	10	—	38.23	—
	10	—	38.30	—
	10	—	38.15	—
	10	13.18	—	—
	10	13.20	—	—
	30	39.85	—	—

With each of the three samples the alcoholic titration requires from 1 to 3 per cent more than one-third of that required in the water titration.

This result might be explained in either of two ways:—That the fluosilicic acid, as sold commercially and as made in the Penfield Offermann method for determining fluorine, may always contain small amounts of free hydrofluoric acid, or the solubility of potassium fluosilicate may be sufficient to allow it to be appreciably acted upon by the alkali used. The latter of these two explanations seems more plausible; for when the end-point has been reached, as shown by the pink of the phenolphthalein, the colour fades out upon short standing, and continues to disappear after successive additions of alkali sufficient to bring back the pink. Upon heating the mixture the hydrolysis goes much further, and practically all of the potassium fluosilicate is converted to fluoride and silica.

TABLE II.

H_2SiF_6 used, cc. of solution.	HF used, grm. of solution.	KCl added. Grms.	NaOH req. Cc.	NaOH theory. Cc.	Diff. Cc.
10	4.8818	3	19.91	21.07	1.16
10	5.6151	1	21.49	22.62	1.13
10	10.2629	1	31.12	32.42	1.30
10	12.2639	1	35.37	36.65	1.28
10	16.3859	1	44.01	45.34	1.33

To test Katz's theory of the absorption of hydrofluoric acid by potassium fluosilicate, 10 cc. portions of fluosilicic acid were mixed with varying amounts of hydrofluoric acid, and these mixtures were titrated, after addition of alcohol and potassium chloride, with approximately 0.3

* From the *American Journal of Science*, xlii, No. 251.

TABLE III.

	KCl used. Gm.	H ₂ SiF ₆ used. Gm.	KCl in filtrate. Gm.	HF used, gm. of solution.	K ₂ SiF ₆ precipitate Gm.	KCl equivalent of K ₂ SiF ₆ . Gm.	H ₂ SiF ₆ equivalent.	KCl by filtering and decomposition.	Total KCl.
a.	0.5090	0.2634	0.2381 (a)	—	0.4006	0.27085	0.2622	—	—
b.	0.5090	0.2634	0.2422	—	0.3979	0.2687	0.2601	—	0.5110
c.	0.5090	0.2634	0.2414	—	0.3991	0.2695	0.2609	—	0.5109
d.	0.5090	0.2634	0.2258 (a)	10	0.4196 (a)	0.2832 (a)	0.2748	—	—
e.	0.5090	0.2634	0.2288	10	0.4169 (a)	0.2824	0.2725	0.2785	0.5073

(a) Calculated.

normal sodium hydroxide. Since the amount of alkali required for each acid separately was known it was easy to calculate what the mixture should require, were there no complications. These results are shown in Table II.

The fluosilicic acid used required for 10 cc. in alcohol, 10.77 cc. of standard alkali. Upon addition of increasing amounts of hydrofluoric acid, that unaccounted for seems to reach a maximum which is equivalent to approximately 1.3 cc. of the alkali used. This would give a ratio of absorption of one molecule of HF for about four of H₂SiF₆ instead of a ratio of 1:1 as Katz found under these conditions.

If the precipitate of potassium fluosilicate formed in the presence of free hydrofluoric acid consisted entirely of potassium fluosilicate and of free hydrofluoric acid which it absorbed, then by determining the potassium in it a measure of the fluosilicic acid originally present would be obtained. Or if a known amount of potassium chloride were added for precipitation and that remaining in the filtrate determined, the difference would be that which was used up in forming potassium fluosilicate. For this purpose a standard solution was made of which 10 cc. contained 0.5090 gm. of potassium chloride. Table III. gives the results of precipitating potassium fluosilicate from a solution of fluosilicic acid with and without hydrofluoric acid being present.

It will be seen that *a*, *b*, and *c* each give a precipitate equivalent to a little less than the theoretical value for fluosilicic acid. This would be expected on account of the appreciable solubility of potassium fluosilicate.

In *d* and *e*, where about 10 grms. of hydrofluoric acid were added, in each case the filtrate contained considerably less of potassium chloride than would have been the case if no potassium had been used up except by fluosilicic acid in forming potassium fluosilicate. In *e* the precipitate weighed 4 or 5 per cent too much. It was decomposed by ammonia, and the solution was filtered to get rid of asbestos and then acidified with hydrochloric acid, and evaporated. The residue was heated with hydrochloric acid to drive off all silica and fluorine and to convert the entire residue to potassium chloride. The residue of potassium chloride so obtained was found to weigh several per cent more than if the potassium had been present in the precipitate only as potassium fluosilicate.

The precipitate of potassium fluosilicate formed in the presence of free hydrofluoric acid contains an excess of potassium salt as well as free hydrofluoric acid, and it is evident that the fluosilicic acid in a mixture of the two acids cannot be estimated by determining the potassium in the precipitate or in the filtrate.

Since the fluosilicic acid carries down with it free hydrofluoric acid and fluorides when it is precipitated in the presence of these, it was determined, if possible, to precipitate the hydrofluoric acid as some insoluble fluoride, and, having thus removed it from the solution, to determine the fluosilicic acid remaining.

Accordingly, to a mixture of fluosilicic and hydrofluoric acids was added a neutral solution of calcium chloride sufficient to precipitate as calcium fluoride all of the fluorine present as hydrofluoric acid. Next was added potassium chloride sufficient to form with the fluosilicic acid, potassium fluosilicate, and to the mixture was added alcohol to make the final solution consist of 50 per cent

alcohol. The precipitate obtained under these conditions was found very difficult to filter, so the mixture was made up to a definite volume, and after allowing to settle the clear supernatant liquid was decanted through a dry filter. Aliquot parts of the total volume were then titrated with standard alkali.

If all of the hydrofluoric acid were actually precipitated as calcium fluoride and all of the fluosilicic acid as potassium fluosilicate, then for each molecule of HF originally present there should be in the filtrate one molecule of hydrochloric acid, and for each molecule of fluosilicic acid two molecules of HCl, according to the reactions,—



Upon titration of this filtrate, therefore, the alkali required should be equal to that which would be required in water solution for the hydrofluoric acid originally present, plus one-third of that fluosilicic acid originally present. Thus the difference between the original water titration and the titration of this filtrate should be just two-thirds of the alkali required in the reaction $\text{H}_2\text{SiF}_6 + 6\text{NaOH} = 6\text{NaF} + \text{Si(OH)}_4 + 2\text{H}_2\text{O}$, and so the amount of fluosilicic acid could be calculated.

Titration made in this manner all tended to run low to about the same extent as those made after simply adding potassium chloride and alcohol to the mixture of the two acids. The explanation of this is probably that an insoluble compound of potassium fluosilicate and hydrofluoric acid is formed even in the presence of soluble calcium chloride.

(To be continued).

BOARD OF SCIENTIFIC SOCIETIES.

At a meeting of the Board of Scientific Societies, held on October 12, 1916, the Board approved the appointment of the following Sub-Committee to consider and report upon National Instruction in Technical Optics:—Mr. Conrad Beck, Mr. F. J. Cheshire, Mr. E. B. Knobel, Sir Philip Magnus, Prof. H. Jackson, Prof. A. Schuster. This Sub-Committee, having given careful consideration to the subject referred to them, reported as follows:—

REPORT OF COMMITTEE APPOINTED TO CONSIDER AND REPORT ON NATIONAL INSTRUCTION IN TECHNICAL OPTICS.

Several attempts have been made during recent years to provide systematic training in Technical Optics, and a scheme prepared by the London County Council will be referred to in this Report. But, before discussing the details of any proposals, it is advisable to form a clear conception of the requirements of the optical trade, and of the organisation of the teaching best adapted to promote the interests of that trade without regard to existing conditions, which no doubt will place some difficulties in the way of the immediate adoption of a thorough-going and satisfactory scheme.

It is necessary at the outset to emphasise one point which is of vital importance. If a perfect organisation for instruction and research in optics could instantaneously

be called into being, some years would necessarily elapse before the trade would appreciably benefit by it, because that trade requires above everything a sufficient supply of men thoroughly trained in the scientific principles underlying the proper construction of optical appliances. Such men are not obtainable at the present moment; they will have to be trained, and this requires time. But the next few years are the years which will determine the future of the industries of the country. To avoid a delay which might prove fatal, it is essential that provision should be made at once to give the trade such assistance and advice as will ultimately be supplied by the body of trained men which, it is hoped, will be available in a few years.

This leads us to our first recommendation. Whatever scheme be adopted, it is essential that it should include the appointment of a highly-qualified scientific man, who will be charged with the organisation and direction of the whole of the teaching. This man, to whom we shall refer as the "Director"—whatever title he may subsequently receive—ought to be appointed at once. Among the duties specially assigned to him in the preliminary period should be that of advising the trade in any difficulties they may encounter. A sufficient staff should be assigned to him for the purpose. The Director should not be attached exclusively to any of the existing institutions.

A further need, which is urgent, is the supply of standard text-books dealing with those parts of optics which at present are greatly neglected in this country; this includes practically the whole of geometrical optics and a large part of technical optics. In our opinion, the quickest and most effective manner of dealing with this requirement is by publishing translations of existing foreign books and abstracts of important papers on the subject.

In defining the range of teaching to be provided, and forming an estimate of the number and type of the students who may avail themselves of the opportunities offered, we must keep in mind that the use of a knowledge of optics is not confined to those intending to enter the optical trade. The Army, the Navy, the Patent Office, and other Government departments employ optical experts. We are informed that the Royal Naval College habitually send some of their ablest young officers to an optical firm, to be instructed in the principles and designs of range-finders, gun-sights, and other optical instruments. Medical men, bacteriologists, surveyors, and nautical men would, also, in many cases, welcome instruction in special branches of optics. We may here refer to the School of Economics, an institution mainly devoted, as its name implies, to a highly specialised branch of knowledge, which derives its practical importance from its connection with matters affecting the welfare of the country. In these respects, it presents a certain analogy with the proposed School of Optics. Experience in this case shows that the instruction given has attracted, from much wider circles than was originally contemplated, students desiring instruction in special departments of economics. It is, therefore, well not to take too narrow a view, but to look upon the practical application of optics as being one of the many points of contact between the industries and pure science. Any advance in its study will hence react beneficially on the advance of the science on which it is based.

We therefore look forward to the establishment of an Optical Institute which would concentrate the efforts of all who are concerned with the manufacture or use of optical instruments. It would bring together the several Optical Societies, who might find a home within its building; it would be the centre for the co-operation of the trade with students and teachers; it should contain a library with periodicals and books on optics.

The general direction of the courses of study should—as is the case in the scheme of the London County Council—be vested in an Advisory Council on which the trade, as well as the optical and learned societies, are represented. It has already been insisted upon that there

should be a Principal or Director who is highly qualified both on the theoretical and practical side, and who would be responsible to the Advisory Council. Full courses of instruction, both in day and evening classes, will be required. The day departments would consist mainly of youths between the ages of fifteen and twenty, who would receive general and technical instruction, including mathematics, physics, chemistry, and practical optical work.

The evening work would be adapted to the requirements—

(1) Of students engaged in the trade during the day-time;

(2) Of advanced students, some of whom would have graduated in science, and would be preparing to occupy the position of managers in optical works;

(3) Of other persons interested in learning the scientific construction or use of optical instruments.

Provision should be made for research work not requiring a highly specialised or expensive plant. Special investigations might be referred to the National Physical Laboratory, or any other laboratory suitable for the purpose.

It is also worth considering whether a good journal or paper should not be published, devoted to scientific instruments and other matters concerned with optics.

We are aware of the difficulties which stand in the way of putting into immediate operation a scheme which would satisfy in a comprehensive manner all the above conditions. It will therefore be necessary to contemplate a transitional period leading up to what we ultimately hope to obtain.

In considering the provisional arrangements, regard must be had to the fact that already some very good work in the training of operatives of different classes is being done at the Northampton Polytechnic Institute, where a certain amount of modern machinery and apparatus has been provided, and young men and women are receiving useful training, the value of which has been recognised by the Government. We may also draw attention to the valuable research work being carried out in King's College, London, under the Glass Research Committee of the Institute of Chemistry. The instruction given at the Northampton Institute should, however, at once be supplemented by more advanced teaching in some convenient institution of University rank. Stress has already been laid on the immediate appointment of a Principal or Director, and there is no reason for delaying the formation of the Advisory Council. So soon as the preliminary work of organisation permits, plans should be prepared for a new building, which, in our opinion, is essential.

The scheme of the London County Council represents a carefully considered attempt to utilise and extend the teaching given in existing institutions and to reconcile conflicting interests. Its object is, therefore, the same as that which we contemplate in the transitional period, and in its main features it seems to differ little from our proposals. It is not with the object of making any captious criticism, but merely to prevent possible misunderstanding, that we desire to point out what seems to us to be serious defects in the details of the scheme.

It is provided that the Imperial College of Science should institute a separate department of technical optics, with a Head who is also to exercise some undefined powers of general supervision over the whole scheme. Being a member of the staff of the Imperial College, he would presumably be appointed by the governing body of that Institution, and primarily be responsible to it. He would have at the same time powers over the course of instruction at another institution that had no voice in his appointment. His relationship to the Advisory Council is not defined, and the proposal in its present form does not seem to us to be conducive to harmonious working. It also seems to perpetuate what, in our opinion, should only be a transitional stage. Our own proposal con-

templates that the appointment of the Director of Studies should be primarily vested in whatever body is constituted as the main governing body.

Another fundamental defect of the scheme is implied in the wording defining the distribution of the work between the Imperial College and the Northampton Institute. Stress appears to be laid on post-graduate work conducted at the Imperial College, and research work is confined to that Institution. If it be meant that the normal course of instruction should begin with a degree course in pure science, and the higher technical teaching should only begin after such a course is completed, we must express our dissent from that view. There may be some cases, no doubt, where a graduate in science will turn his mind towards technical optics, and provision should be made for him; but the centre of gravity of the institution must be a course extending over two or three years, in which teaching in science is, *ab initio*, directed towards the necessities of its optical applications. As regards research work, the teachers in any institution which may be built, or during the transitional period at the Northampton Institute, should be of sufficient standing to be able to conduct research work, and though no expensive or elaborate plant need be supplied, and such research work need not form a prominent part of the activity of the Institute, it is not advisable to lay down any hard or fast lines as to where researches are to be carried out. Special investigations, as has already been said, will probably be largely concentrated at the National Physical Laboratory, but they also should not necessarily be confined to any one place.

In conclusion, we may sum up the requirements which appear to us to require immediate attention:—

1. The appointment of a supervising representative Council.
2. The appointment, under the proposed supervising Council, of an administering Director, with special duties during the transitional period, which will include advice to the trade and the organisation of the different parts of the curriculum.
3. The translation of suitable works and the abstracting of other important publications on technical optics.
4. Pending the erection of a suitable building, the organisation of day and evening courses at the Northampton Institute, and arrangements for higher instruction at some other institution of University rank.

The term "Technical Optics" throughout the Report is intended to include the chemical composition and manufacture of glass.

The Committee is willing to give further advice with respect to the selection of books for translating or abstracting, and any other matters connected with subjects referred to in the Report.

(Signed) ARTHUR SCHUSTER, *Chairman*.

This Report was received and approved by the Board at a meeting on January 24, 1917.

(Signed) J. J. THOMSON, *Chairman*.

SULPHATE OF AMMONIA ASSOCIATION.

THE following circular letter has been issued to sulphate of ammonia makers, with reference to the price of sulphate of ammonia fixed by the Government for home consumption.

DEAR SIR,—You will remember that at the Meeting of Sulphate of Ammonia Makers held on November 28, 1916, at these offices, to which all makers of sulphate of ammonia were invited, the under-mentioned Committee was appointed to consider "how the agricultural needs of the country with regard to sulphate of ammonia can best be met at the present time."

After several meetings this Committee, which has come to be known as the "Equalisation Committee," succeeded in drafting a scheme which would enable makers in agricultural districts to sell the whole of their make for home consumption, but at the same time give them a fair share in the higher prices obtainable for export, and thus secure that the needs of the country would be met in the most economical manner.

In the meantime, the change of Government occurred, and the new Food Controller appointed individual members of the Equalisation Committee to act as an Advisory Committee to the Ministry of Food with regard to questions affecting the production and distribution of sulphate of ammonia.

In view of the complaints of agriculturists regarding the difficulty in obtaining sulphate of ammonia and the pressure they were bringing to bear on the new Agricultural Departments of the Government to reduce the price, it was necessary, firstly, to show the Government that sulphate of ammonia makers had a plan ready to deal with the situation, and, secondly, to make every effort to secure that due consideration should be given by the Government to manufacturers' interests.

The scheme was therefore submitted to the Food Controller, and a number of meetings were held at which the interests of both agriculturists and manufacturers were fully and frankly discussed.

As a result, at a final meeting held on February 10, the Advisory Committee were informed that the War Cabinet, having considered the whole question, had decided that, on or after Monday, February 12, 1917, sulphate of ammonia is to be sold at the price of £16 per ton, 24½ per cent basis, in maker's bags, net cash, delivered at the consumer's station in any part of Great Britain and Ireland. The price to consumers who take delivery at maker's works for conveyance otherwise than by railway to remain at £15 10s. per ton on the above terms.

Further, that the Government were prepared to pay to the Advisory Committee, 10s. per ton in respect of every ton of sulphate of ammonia sold, on or after February 12, 1917, for home agricultural use, at not exceeding £16 per ton as above if failed to consumer's station.

The Food Controller lays on the Advisory Committee the obligation to give effect to an approved scheme for regulating the distribution of supplies to farmers in all parts of the United Kingdom, and has approved of the general principle embodied in the scheme submitted to him by the Equalisation Committee.

This scheme will be circulated among makers as soon as the modifications rendered necessary by the new prices have been introduced into it. The most important of these modifications will be a provision for equalising the amount of railway carriage payable by each maker.

The Advisory Committee will advise the Food Controller as to the works from which it is advisable that sulphate of ammonia should be exported in the event of further export being permitted at some future date.

In the meantime, in view of the fact that all export has been stopped, we advise every manufacturer to book all orders which do not involve payment of more than 10s. per ton railway carriage. Where the carriage exceeds 10s. per ton they should first communicate with the Secretary to the Sulphate of Ammonia Advisory Committee, 84, Horseferry Road, London, S.W.

Makers should, in every case, apply to the head rates office of railway companies for the rates—these are more likely to be correct than those quoted locally.

Railway accounts will have to be produced when claiming a share in the Government contribution to the Advisory Committee, and should therefore be preserved. An announcement will be made in due course as to when claims are to be sent in.

The above-mentioned prices are defined as the retail prices to be charged by both manufacturers and merchants to consumers for cash.

In view of the important part played by corn and manure

merchants, manure mixers, and farmers' co-operative trading societies as distributors, and the large extent to which sulphate of ammonia makers will be dependent on their good will after the war, the Advisory Committee recommend that, as heretofore, 10s. per ton should be allowed to these traders on the above prices.

The new prices apply only to sales made on or after February 12, 1917.

In conclusion, we feel we can confidently appeal to all manufacturers for their loyal support and co-operation in giving effect to the new regulations, which should still further popularise sulphate of ammonia among farmers.—Yours faithfully,

D. MILNE WATSON.

Chairman Sulphate of Ammonia Advisory Committee.

Names of the Members of the Committee:—D. Milne Watson (Chairman), Wm. Fraser, E. J. George, W. R. Hann, N. N. Holden, A. K. McCosh, Alderman F. S. Phillips, A. Stanley, F. C. O. Speyer (Secretary).

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, February 8, 1917.

Sir J. J. THOMSON, O.M., President, in the Chair.

PAPERS were read as follows:—

"Dynamics of Revolving Fluids." By Lord RAYLEIGH, O.M., F.R.S.

The fluid is supposed to be devoid of viscosity, and the motion to be at all times symmetrical about an axis. In accordance with Kelvin's general theorem the circulation remains constant for each ring of fluid. In equilibrium the rings of fluid must be so arranged that the circulation is in cylindrical layers, and if the equilibrium is to be stable the circulation must increase outwards. An example is taken from fluid originally rotating like a solid and enclosed by coaxial cylindrical walls. If these close in, a simple vortex motion of increasing intensity is superposed, and the difference of pressures at the walls also increases.

When the motion is in three dimensions, exact solutions are hardly practicable, but some general considerations are appended, suggested by a recent paper of Dr. Aitken.

"Deflection of the Vertical by Tidal Loading of the Earth's Surface." By Prof. HORACE LAMB, F.R.S.

This subject has of late excited renewed attention owing to its bearing on observations of lunar disturbance of gravity. The present paper, after discussing a few typical problems, goes on to examine the effect of one or two considerations which have been hitherto left out of account, so far as the author is aware, in such calculations. In the first place, owing to the deformation of the surface and the altered distribution of density, an additional horizontal component of force on the pendulum is introduced. A more important point is that the action of gravity in resisting the deformation is ignored. It is true that the corrections involved are under certain conditions negligible, but they are of some theoretical interest, and it is found that at great distances from the load, and therefore in all cases of a widely distributed load, they may attain considerable relative importance.

In attempting to estimate the effect of gravity it has been found convenient, in order to avoid difficulties not altogether of a mathematical kind, to limit the investigation to the case of incompressibility. In the first instance, also, the disturbance in the field of gravity has been neglected in calculating the strains.

When the alteration of the field is taken into account a curious point arises. For mathematical simplicity the

"earth" has been regarded, as is usual in such investigations, as flat and infinitely extended. It appears that in such a case the surface would be unstable, whatever the degree of rigidity, for disturbances exceeding a certain wave-length. This critical wave-length is, however, enormous, and reasons are given for the view that inferences can legitimately be drawn from the results as to the character of the effects actually produced.

"Spontaneous Generation of Heat in Recently Hardened Steel." By C. F. BRUSH and Sir R. HADFIELD, F.R.S.

Steel specimens of different composition were hardened and then placed in Dewar vacuum jars so arranged as to have equal thermal insulating efficiency. These were placed inside an air-tight cylinder of thin copper, embedded in granulated coke placed in another box surrounded by an air space and a further box. The special apparatus employed is fully described in the paper.

Carbon steel, also nickel-chromium steel specially susceptible to hardening, and other steels were then quenched from hardening temperatures, and when cold placed in the vacuum jars and the temperatures carefully recorded in the manner described in the paper. It was found that there was an evolution of heat of minute but appreciable quantity.

As regards the bearing of this research as applied to industrial practice, whilst the rise of temperature is minute and may not have any direct bearing upon hardening results, the curious phenomenon noticed throws light upon the serious stresses and strained condition of the material produced in large masses of steel during hardening operations.

SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS.

Annual General Meeting, February 7, 1917.

Mr. GEORGE EMBREY, President, in the Chair.

THE PRESIDENT delivered his Annual Address. The following were elected Officers and Council for the ensuing year:—

President—George Embrey.

Past-Presidents serving on the Council (limited by the Society's Articles of Association to eight in number)—Leonard Archbutt, Edward J. Bevan, A. Chaston Chapman, Bernard Dyer, Otto Hehner, R. R. Tatlock, E. W. Voelcker, and J. Augustus Voelcker.

Vice-Presidents—H. G. Colman, J. T. Dunn, C. A. Hill.

Hon. Treasurer—Edward Hinks.

Acting Hon. Treasurer—E. W. Voelcker.

Hon. Secretaries—P. A. Ellis Richards and E. Richards Bolton.

Other Members of Council—W. T. Burgess, T. W. Glass, H. G. Harrison, G. N. Huntly, P. H. Kirkaldy, Stevenson J. C. G. Macadam, William Macnab, W. Partridge, W. H. Roberts, E. Russell, H. L. Smith, J. Webster.

The meeting having been resolved into an Ordinary Meeting,

A certificate was read for the first time in favour of Mr. Hubert Charles Siegfried de Whalley.

A certificate was read for the second time in favour of Prof. Alfred Francis Joseph, D.Sc., F.I.C.

Mr. Gerrard W. Baker was elected a member of the Society.

The following papers were read:—

"Quantitative Estimation of Mercury in Organic Compounds." By J. E. MARSH and O. G. LYE.

The authors describe a modification of the method of estimating mercury in organic compounds by combination with quicklime, by means of which the mercury is separated as a single globule without admixture of any tarry

or crystallisable distillate, such as is sometimes obtained with aromatic derivatives.

"*The Shrewsbury and Knapp Process for the Detection of Coconut Oil.*" By G. D. ELSDON.

The author has studied the method of Shrewsbury and Knapp (*Analyst*, 1910, xxxv., 385) for the determination of coconut oil in mixtures, and also the modification suggested by Revis and Bolton (*Analyst*, 1911, xxxvi., 334), but it has not been found possible to obtain concordant results by either method. In the present paper the suggestions of Revis and Bolton are further modified by the use of alcohol of sp. gr. 0.9200 and by thoroughly drying the cake of fatty acids before solution in alcohol, experimental evidence being given in support of these changes. In the author's hands the proposed process gives excellent results.

"*Detection of Rose Petals in Blue Pill.*" By WILLIAM PARTIDGE.

The test proposed for the detection of rose petals in blue pill by M. Dechan and T. Maben ("Year-book of Pharmacy," 1884, p. 566; and *Pharm. Journ.*, Sept. 20, 1884) depends on the production of a bright pink colour when the pill mass is heated with strong acetic acid. The test is unreliable. Even should a newly made pill give it, which is not always the case, the other constituents of the pill in time destroy the pigment on which the test depends. The presence of rose petals can be determined by microscopical examination, sufficient of their structure remaining after manufacture to permit identification. The characteristic smell persists for at least a year.

NOTICES OF BOOKS.

A Handbook for Cane-sugar Manufacturers and their Chemists. By GUILFORD L. SPENCER, D.Sc. Fifth Edition. New York: John Wiley and Sons, Inc. London: Chapman and Hall, Ltd. 1916. Pp. xv+529. Price 15s. net.

In the fifth edition of this book the information relating to the manufacture of cane-sugar is much fuller than in the earlier editions, the whole process being described in detail from the arriving of the cane at the factory to the production of the refined sugar. The processes of refining described are those which are adopted in American refineries, as are the methods of technical and chemical control of the refinery. The analysis of sugar is, as before, very comprehensively treated, general routine work being described in full with explanations of methods of calculation and of the purchase of the cane on the basis of its analysis. A useful chapter on some abnormal constituents of cane-sugar products is included. Many of the tables in the fifth edition are new, and they give all the numerical information that could possibly be wanted for analytical purposes. The book will be found a very useful addition to the library of the sugar-chemist, who will find that it contains clear accounts of all the analytical work he is usually called upon to perform, besides providing him with an excellent account of methods of manufacture.

Atoms. By JEAN PERRIN. Authorised Translation by D. LL. HAMMICK. London: Constable and Co., Ltd. 1916. Pp. xiv+211. Price 6s. net.

THERE could be no better exponent of our present-day knowledge of the nature of the atom and molecule than Prof. Perrin, whose work "*Les Atomes*" has won worldwide recognition as the best and most authoritative short treatise on the subject. This book is a translation of the fourth edition of his work. Prof. Perrin's aim was to

show how the modern doctrine of the atom explains "the complications of the visible in terms of invisible simplicity," and this aim is fulfilled in a masterly manner. The remarkable experiments devised by the author and others in the investigation of the structure of the atom are described fully, and the reader cannot fail to be struck by the thought that they form part of some of the most beautiful work that has ever been done by man in the investigation of nature. The chapters on the Brownian movement are models of lucidity and directness, and the interest is sustained in such a way that it can easily be imagined that the student to whom the facts and theories were new would be unable to resist reading on from page to page until the whole tale was told and he was brought face to face with the triumphant conclusion of the agreement of the values of $N/10^{22}$ obtained by the most widely different methods. The book is one which should be carefully read by teachers and students of chemistry, and it is so exceedingly clearly written that any student who has been through an intermediate course of inorganic chemistry could not fail to understand and benefit by it.

MEETINGS FOR THE WEEK.

TUESDAY, 27th.—Royal Institution, 3. "The Strength and Structure of Metals," by Prof. W. E. Dalby.

— Royal Society of Arts, 4.30. "Imperial Assets and How to Use Them," by Alfred Bigland, M.P.

WEDNESDAY, 28th.—Royal Society of Arts, 4.30. "The War and our Supply of Drugs," by Francis A. Hocking.

— Society of Chemical Industry (Liverpool Section), 6. (Musparr Lecture, The University, Brownlow Hill). "The Modern Whale Oil Industry," by W. Mansbridge.

THURSDAY, March 1st.—Royal Institution, 3. "Memorial Art To-day," by Prof. E. S. Prior.

— Chemical Society, 8. "Effect of Heat and Oxidation on Linseed Oil," by J. A. N. Friend. "Acyl Derivatives of Paradiazobenzene," by G. T. Morgan and A. W. H. Upton.

FRIDAY, 2nd.—Royal Institution, 5.30. "Cellulose and Chemical Industry (1866-1916)," by C. F. Cross.

SATURDAY, 3rd.—Royal Institution, 3. "The Pronunciation of English at the Time of Shakespeare," by D. Jones, M.A.

NOBEL'S EXPLOSIVES COMPANY, Ltd., ARDEER FACTORY, STEVENSTON.

There are at present several vacancies on the Staff of the above Factory for men suitable for training for the control of manufacture.

Applicants, who must be qualified Chemists, preferably possessing a University degree or its equivalent, should submit full details of their training and experience to THE MANAGER, Research Section, Ardeer Factory, Stevenston.

CITY and COUNTY BOROUGH of BELFAST.

The Library and Technical Instruction Committee invite applications for the Position of TEMPORARY LECTURER AND DEMONSTRATOR in CHEMISTRY in the MUNICIPAL TECHNICAL INSTITUTE, BELFAST.

Salary £160 per annum.

The appointment is for the duration of the War.

Applications will be received from women as well as from men, but in the case of men applications will only be considered from those ineligible for Military service.

Particulars of the Duties and Conditions of Appointment, together with Form of Application, may be obtained from the undersigned, with whom applications (on the special form provided for the purpose) must be lodged not later than Noon on WEDNESDAY, MARCH 7, 1917.

Applications should be accompanied by copies of three recent testimonials (original testimonials must not be sent).

CANVASSING IS STRICTLY FORBIDDEN, AND WILL DISQUALIFY.

Municipal Technical Institute;
Belfast.

THE PRINCIPAL.

THE CHEMICAL NEWS

VOL. CXV., No. 2988.

CHEMISTS IN WAR.

By R. B. PILCHER,

Registrar of the Institute of Chemistry in Great Britain and Ireland.

OWING to the conditions of modern warfare chemists have been more than ever in request. To give a full account of their work, if it were possible, would be imprudent, but it is well to place on record a statement confined to what it is permissible to relate, giving some indication of the importance of the profession of chemistry to the nation in these times. It may be doubted if the general community realises that the chemist plays a part in the production of all iron, steel, copper, and other metal, of every explosive, of cloth, leather, rubber, glass, and material of war generally, and that his help is no less necessary in connection with the supplies of food, pure water, and medicine.

The Government has secured the guidance of chemists and other men of science to assist in the investigation of suggestions and inventions and to bring their knowledge and experience to bear on measures and devices of offence and defence, while apart from those acting in an advisory capacity, chemists have been called for service in the field as well as in the factory. In such times there is a demand for the solution of problems of an unusual character which can only be entrusted to men of the highest scientific training, with initiative and foresight.

So much had we come to rely on foreign sources of supply for many of our needs, that means had to be found for dealing promptly and efficiently with difficulties some of which, unless overcome, threatened serious disaster. The chemists of the country have not been found wanting.

The laboratories of our universities and colleges have become small factories for the preparation of drugs and medicaments, and many institutions have been entrusted with the examination of materials used in the manufacture of explosives. The measures taken in this emergency secured uniformity in method and the standardisation of processes which would otherwise have been difficult to attain. Under the supervision of their professors, students unfit for service with the colours have been helping the country and at the same time gaining useful experience.

Several hundred chemists have been engaged for assistance in the laboratories and in the works of Government and controlled establishments supplying armaments, munitions, and other materials of war. Many of these have found an opportunity of helping the country through the registers maintained by the Institute of Chemistry and other societies for this purpose. In cases where the number of men having technical experience in some branches was limited, the authorities have made arrangements for probationary training, so that their services should be available when required in new factories.

The staffs of the chemical departments of Woolwich Arsenal and other Government factories have been considerably augmented, as also that of the Government Laboratory, which, as the recently published report shows, has been largely responsible for the examination of foodstuffs and many other requirements of the Expeditionary Forces.

In previous wars the authorities have considered officers of the R.A.M.C. sufficiently trained for all necessary military duties involving chemical knowledge, but in the present conflict, with an unprecedented demand for

medical men, qualified chemists have volunteered in such numbers as to give practical force to the suggestion that they should be engaged for the purification and examination of water supplies and for dealing with matters of hygiene requiring chemical knowledge. As a result many have been appointed to commissions and engaged for scientific work, not only with the R.A.M.C., but also with the A.S.C., A.O.D., and other units. Attached to various forces at home, with the armies on the Continent and in Africa, chemists have thus rendered valuable service.

In consequence of methods of offence initiated by the enemy, such as the employment of poisonous gases, there arose a further demand for men with training in chemistry for service in the field. For the duties involved the authorities deemed it expedient to enlist men with such training, rather than entrust them to men without any scientific knowledge, and the unit thus formed is a fighting force. With the assistance of the universities and technical colleges and the various bodies interested in chemistry, an entirely new force was brought into existence. At that time there was no question of compulsion, yet it was raised with little difficulty, being subsequently augmented, by the addition of other troops. The men went voluntarily, and were sent abroad at very short notice, and after short training went into action. The officers were mainly selected from chemists who already held commissions, while sergeants and corporals with knowledge of chemistry were transferred from other units. That they did their work well is shown by the following abstracts from despatches of Lord French and Sir Douglas Haig:—

LORD FRENCH, October 15, 1915.

"Owing to the repeated use by the enemy of asphyxiating gases in their attacks on our positions, I have been compelled to resort to similar methods; and a detachment was organised for this purpose, which took part in the operations commencing on September 25 for the first time.

"Although the enemy was known to have been prepared for such reprisals, our gas attack met with marked success, and produced a demoralising effect in some of the opposing units, of which ample evidence was forthcoming in the captured trenches.

"The men who undertook this work carried out their unfamiliar duties during a heavy bombardment with conspicuous gallantry and coolness; and I feel confident in their ability to more than hold their own should the enemy again resort to this method of warfare."

SIR DOUGLAS HAIG, May 19, 1916.

"The valuable nature of the work performed by the officers of the Central Laboratory and the chemical advisers with the Armies in investigations into the nature of the gases and other new substances used in hostile attacks, and in devising and perfecting means of protecting our troops against them, is deserving of recognition. The efforts of these officers materially contributed to the failure of the Germans in their attack of December 19, 1915, as well as in the various gas attacks since made."

SIR DOUGLAS HAIG, December 23, 1916.

"The employment by the enemy of gas and of liquid flame as weapons of offence compelled us not only to discover ways to protect our troops from their effects, but also to devise means to make use of the same instruments of destruction. Great fertility of invention has been shown, and very great credit is due to the special personnel employed for the rapidity and success with which these new arms have been developed and perfected, and for the very great devotion to duty they have displayed in a difficult and dangerous service. The Army owes its thanks to the chemists, physiologists, and physicists of the highest rank who devoted their energies to enabling us to surpass the enemy in the use of a means of warfare

which took the civilised world by surprise. Our own experience of the numerous experiments and trials necessary before gas and flame could be used, of the great preparations which had to be made for their manufacture, and of the special training required for the *personnel* employed, shows that the employment of such methods by the Germans was not the result of a desperate decision, but had been prepared for deliberately.

Since we have been compelled, in self-defence, to use similar methods, it is satisfactory to be able to record, on the evidence of prisoners, of documents captured, and of our own observation, that the enemy has suffered heavy casualties from our gas attacks, while the means of protection adopted by us have proved thoroughly effective."

High qualifications were unnecessary for the work of the rank and file, but many very competent men joined, and it may be mentioned incidentally that it was remarked on an early occasion that generally speaking the best qualified chemists proved the best soldiers. The majority of the university graduates and men possessing recognised diplomas, who originally enlisted as corporals, subsequently received commissions, and when the force was more completely organised a considerable number were withdrawn and transferred to the Ministry of Munitions in order that their services might be available in work of a more scientific character.

Mention should also be made of the fact that during the campaign against the rebels in South Africa and the Germans in South-West Africa chemists were attached, on the personal order of General Botha, to the different brigades and rendered valuable service.

From the experience gained in the campaign it is clearly advisable that the State should have control of such an organisation of professional chemists as to ensure at any time their efficient service in the many requirements of the naval, military, and air forces. In addition to competent chemical advisers of undoubted standing, the following appear to be essential:—

Chemists to control the manufacture of munitions, explosives, metals, leather, rubber, oils, gases, food, drugs.

Chemists for the analysis of all such materials and for research.

Chemists, on active service, to assist in the control of water supplies, in the detection of poison in streams, in the analysis of water and food, in the disposal of sewage, and in other hygienic matters.

Chemists, both at home and on active service, to assist in devising safeguards against enemy contrivances of a scientific nature, and methods of offence to meet the same, as well as for the instruction of troops in such matters.

It has been called a "chemists' war" and an "engineers' war." Many regard it largely as a conflict between the men of science of the countries engaged. Our chemists have not been dismayed at that, but it is impossible to foresee to what limits beyond accepted tenets the enemy is prepared to go in the application of science to warfare, and we cannot reproach ourselves with having set an example of frightfulness.

To sum the matter up, chemists have met the situation with a spirit of true patriotism and have been promptly organised for the service required of them. It is not too much to hope that, as the discoveries of science have been applied to the destruction of humanity, they may be devoted more and more to the furtherance of the arts of peace, to the uplifting of civilisation and the pacification of the world.

During the war, in spite of the shortage of labour, considerable additions have been made to the large manufacturing concerns throughout the country in the extension of factories, both for the production of things hitherto obtained from abroad and for the requirements of the war.

One important lesson which on no account must be lost sight of is that the country must be self-supporting in all such requirements.

The chemists engaged in connection with the production of materials of war include a large number who were previously occupied in works which have passed under Government control. Most of these were members of the Institute or graduates in science and many were teachers, who thus obtained an insight into operations on a manufacturing scale. If they return to teaching, this experience will have broadened their views; but many will no doubt prefer to remain in industry. Of those with the forces, probably the majority will return to their former work. In any case, many good British chemists should be available for the furtherance of British industry.—*Proceedings of the Institute of Chemistry.*

THE SPECIFIC CONDUCTIVITY OF PURE WATER IN EQUILIBRIUM WITH ATMOSPHERIC CARBON DIOXIDE.*

By JAMES KENDALL.

(Concluded from p. 88).

7. The Solubility of Carbon Dioxide in Water.

THE old and approximate absorption data of Bunsen (*Ann.*, 1855, xciii., 1) may be discarded in favour of the more recent and accurate determinations of Bohr and Bock (*Ann. Phys.*, 1891, xlv., 318) and cf. Just (*Zeit. Phys. Chem.*, 1901, xxxvii., 342). Bohr and Bock obtained the following solubility values for the temperatures considered in this paper:—

	Absorption coefficient.	Solubility in g. mols. per litre.
0°	1.713	0.0764
18°	0.928	0.0414
25°	0.759	0.0338

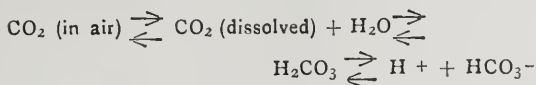
The second column indicates the number of volumes of carbon dioxide (reduced to 0° and 760 mm.) absorbed by one volume of water at the given temperature when the partial pressure of the gas is one atmosphere (760 mm. Hg). In the third column the concentration of the saturated solution under the same conditions is shown. The values of Just are in close agreement with these.

From the above figures the concentration of the saturated solution under atmospheric conditions (carbon dioxide 3.53 parts in 10,000 by volume) can be calculated. It may be noted that variations in the atmospheric pressure—which may amount to about 3 per cent of the total pressure, affecting the partial pressure of carbon dioxide in the same ratio—may be neglected in this calculation, owing to the greater uncertainty in the "standard value" of 3.53 parts in 10,000 for the carbon dioxide content of the atmosphere. The deviations of carbon dioxide from Boyle's law for pressures below atmospheric may also be left out of consideration for the same reason (see Washburn, "Principles of Physical Chemistry," 1915, p. 30). The partial pressure of carbon dioxide in the air may therefore be taken as equal to—

$$760 \times 3.53 \times 10^{-4} \text{ mm. Hg.}$$

Henry's law in its simple form cannot be employed in our calculations, since at the high dilutions involved the degree of ionisation of carbonic acid becomes considerable. It is here that Knox and others have gone astray in estimating the concentration of the solution in equilibrium with the atmosphere (compare Walker and Cormack, *Journ. Chem. Soc.*, 1900, lxxvii., 12). The complete equilibrium series:—

* From the *Journal of the American Chemical Society*, xxxviii., No. 8.



leads for dilute solutions* to the equations—

$$\text{conc. CO}_2 \text{ (in air)} = k_1 \text{ conc. CO}_2 \text{ dissolved} = k_2 \text{ conc. H}_2\text{CO}_3 = k_3 \text{ conc. H}^+ \text{ conc. HCO}_3^-,$$

in which k_1 , k_2 , and k_3 are constants for any given temperature. The fact that the non-ionised solute exists partly as CO_2 and partly as H_2CO_3 does not complicate our calculations at all, since, as will be seen from the above equations, the ratio:—(conc. CO_2)/(conc. H_2CO_3) in dilute solutions will be a constant, k_2/k_1 . The series of equilibria therefore simplifies to the following relationships:—

(1) p/C_n = constant; where p is the partial pressure of CO_2 , C_n the concentration of the total non-ionised solute.

(2) C_i^2/C_n = constant; where C_i is the concentration of the ionised solute.

These may be further condensed into the simple equation:— C_i^2/p = constant, whence it follows that the specific conductivity of a solution of carbonic acid is proportional to the square root of the partial pressure of carbon dioxide under which it exists. The specific conductivities of the solutions in equilibrium with the air, in which the partial pressure of CO_2 is 3.53×10^{-4} atmospheres, can therefore readily be obtained for the three temperatures of 0° , 18° , and 25° by combination of the results of Table IV. with those of the present section.

For purposes of comparison, the complete solubility and ionisation values for these temperatures, under partial pressures of CO_2 of one atmosphere and 3.53×10^{-4} atmospheres, respectively, are given in Tables VIII. and IX. All concentrations are expressed in mols. per litre.

TABLE VIII.—Solubility of CO_2 in Water ($p = 1 \text{ Atm.}$).

T.	Conc. "total non-ionised" solute.	Conc. ionised solute.	Total concentration.	Per cent ionisation.
0°	7.63×10^{-2}	1.3×10^{-4}	7.64×10^{-2}	0.16
18°	4.13×10^{-2}	1.1×10^{-4}	4.14×10^{-2}	0.26
25°	3.37×10^{-2}	1.1×10^{-4}	3.38×10^{-2}	0.33

TABLE IX.—Solubility of CO_2 in Water ($p = 3.53 \times 10^{-4} \text{ Atm.}$).

T.	Conc. "total non-ionised" solute.	Conc. ionised solute.	Total concentration.	Per cent ionisation.
0°	2.69×10^{-5}	2.46×10^{-6}	2.94×10^{-5}	8.4
18°	1.46×10^{-5}	2.13×10^{-6}	1.67×10^{-5}	12.8
25°	1.19×10^{-5}	2.05×10^{-6}	1.40×10^{-5}	14.7

It will be seen that the concentration of the non-ionised portion of the solute decreases rapidly as the temperature rises. In the case of the ionised portion, however, the decrease is but slight, the diminution in the solubility being almost counterbalanced by the increase in the ionisation constant. The last column shows that the degree of ionisation of the saturated solution under atmospheric conditions is considerable.

8. The Specific Conductivity of the Saturated Solution.

The specific conductivity of pure water in equilibrium with atmospheric carbon dioxide at the temperatures of 0° , 18° , and 25° can be calculated directly from the above tables. It may be noted that the specific conductivity of the water itself under these conditions becomes quite negligible in view of the relatively large hydrogen-ion concentration of the solute.

It will be seen that, while the concentration of the ionised solute decreases slowly with rise of temperature, the ionic mobilities increase at a greater rate, hence the

specific conductivity of the saturated solution, as shown in the last column of the table, increases with the temperature. The degree of accuracy of these values, taking into account the errors inherent in the standard value for the CO_2 content of the atmosphere, may be stated as ± 5 per cent.

TABLE X.—Calculated Conductivity of Water in Equilibrium with CO_2 of Air.

T.	Dilution of saturated soln.	Concentration of ionised solute, $A \approx \text{H}_2\text{CO}_3$	Specific conductivity.
0°	34,000 litres	2.46×10^{-6}	264.0×10^{-6}
18°	60,000 litres	2.13×10^{-6}	354.0×10^{-6}
25°	71,400 litres	2.05×10^{-6}	393.4×10^{-6}

We may now proceed to the final step of the investigation—the comparison of the calculated values with those obtained by direct conductivity measurements. In the following table the figures for the specific conductivities of samples of carefully purified water in equilibrium with a normal laboratory atmosphere are collected. Measurements were carried out in each of the four laboratories already mentioned, at the three temperatures 0° , 18° , and 25° . The method of preparation of the conductivity water was the same in all cases—a single distillation from ordinary tap water to which a few cc. of Nessler's solution had been added. (The preparation of conductivity water will be found fully described in a later paper). The water so obtained was allowed to stand exposed to the ordinary laboratory atmosphere, and, after it had rapidly come to equilibrium with this, was found to give readings which were practically independent of the time. The conditions in each laboratory during the measurements were kept as nearly as possible the same as in the determination of the carbon dioxide content of the atmosphere. The conductivity work was carried out in small cells of the Arrhenius type in the usual manner.

TABLE XI.—Measured Conductivity of Water in Equilibrium with CO_2 of Air.

Laboratory.	Specific conductivity. (Reciprocal ohms $\times 10^{-6}$).		
	T. = 0° .	T. = 18° .	T. = 25° .
University of Edinburgh	—	0.75–0.80	0.85–0.90
Technological Institute, Petrograd	0.60–0.70	0.80–0.85	0.85–0.90
Nobel Institute, near Stockholm	—	—	0.75–0.80
Columbia University, New York City	0.60–0.65	0.70–0.80	0.75–0.85

The variations in the measured values are such as would be expected from the variations in the carbon dioxide content of the different laboratories (compare Table VII.). The concordance of the values with those calculated is extremely satisfactory, as may be seen by comparison with the figures shown in the last column of Table X. The agreement obtained is, indeed, so striking as to warrant an emphatic repetition of the conclusion drawn by Walker and Cormack from their investigations, that "we may assume with confidence that carbon dioxide is the only substance in the atmosphere which confers conductivity on water" (Journ. Chem. Soc., 1900, lxxvii., 12).

Supplementary evidence in confirmation of the above assertion will be found in another paper, where the conductivity measurements of other observers on carefully purified water are collected and discussed. It will also be shown that solubility and electromotive force data support the assumption that the purest distilled water of the laboratory is, in point of fact, a saturated solution of carbonic acid under the existing atmospheric conditions. The significance of this in the interpretation of conductivity determinations at very high dilutions will then be examined in detail for electrolytes of different types.

* Where the partial pressure of carbon dioxide is small and the concentration of the water in the solution has not been changed appreciably by the addition of the solute.

9. Summary.

Exact values have been obtained for temperatures of 0°, 18°, and 25°, for the following quantities necessary in the calculation of the specific conductivity of pure water in equilibrium with atmospheric carbon dioxide:—(a) The ionisation constant of carbonic acid; (b) the mobility of the hydrogen carbonate ion; (c) the carbon dioxide content of the atmosphere; (d) the solubility of carbon dioxide in water under atmospheric conditions.

The specific conductivity of a solution of carbonic acid at any given temperature is shown to be proportional to the square root of the partial pressure of carbon dioxide under which it exists.

The values for the specific conductivity of pure water in contact with air, derived with the use of the above data, are, for each temperature considered, practically identical with the directly-measured conductivity values.

The conclusion is drawn that carefully purified conductivity water really consists of a saturated solution of carbonic acid under the partial pressure of the carbon dioxide in the atmosphere, and contains no other conducting impurities in appreciable quantity.

In a following paper some practical applications of this result in the correction of conductivity determinations at high dilutions will be developed, and further evidence of its validity will be brought forward.

A STUDY OF THE SEPARATION OF HYDROFLUORIC ACID AND FLUOSILICIC ACID *

By J. G. LINWIDDIE,

(Concluded from p. 92).

IN a second series of experiments, to a solution of the mixed acids calcium chloride was first added, and to an aliquot part of the clear liquid was added potassium sulphate and alcohol. The potassium ion should form potassium fluosilicate, and the sulphate ion calcium sulphate which with 50 per cent alcohol is sufficiently insoluble not to decompose the potassium fluosilicate when the solution is made neutral with alkali. The results here were low to about the same extent as in the former series of experiments.

This method of making a mixture containing a precipitate up to a definite volume and using an aliquot part of the clear liquid is not to be recommended unless the precipitate is very small, and it is impossible to filter and wash it; therefore other insoluble fluorides such as lead fluoride were tried, but the precipitates were just as hard to filter, and no better results were obtained.

Since other methods failed, and since calcium fluoride seemed to be more suitable for the removal of fluorine than other fluorides because of its greater insolubility, it was determined to find some method of precipitating this compound in a form capable of being filtered.

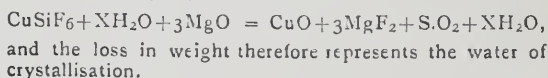
The expedient of Rose, which is to precipitate calcium carbonate together with calcium fluoride, was obviously of no value since the carbonate would decompose the fluosilicate and form calcium fluoride. Calcium sulphate, while being rather insoluble in water, is more soluble than calcium fluoride. Therefore it was thought that if an excess of pure powdered calcium sulphate were added to a solution of sodium fluoride the more insoluble calcium fluoride would continue to form at the expense of the sulphate until all of the fluoride was precipitated as calcium fluoride. There should then remain a precipitate of calcium fluoride mixed with the excess of calcium sulphate.

Upon trial, the precipitate formed in the above manner by the use of calcium sulphate was found to be quite easy to filter and wash, obtaining clear filtrates. A solution containing hydrofluoric acid and fluosilicic acid was now

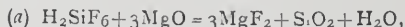
treated with calcium sulphate, and, after stirring well and allowing to stand, the precipitate was filtered and washed. To the filtrate was added alcohol and potassium chloride, and then the free acid was neutralised with standard sodium hydroxide. The results here were low, just as in the previous attempts, and the explanation is very probably that calcium fluoride is sufficiently soluble in the free acid present to dissolve partially and to form in the filtrate free hydrofluoric acid upon addition of the alcohol, and this would then be absorbed by the potassium fluosilicate. If sodium acetate is added in order to decrease the acidity of the solution before addition of calcium sulphate, then the filtrate continues to require alkali very much beyond the amount required by theory. It is probable that in very weakly acid solutions the calcium sulphate acts on the fluosilicic acid to form calcium fluoride, and this would account for the excess of alkali required as follows:—



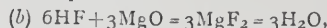
Finally, the method of Stolba for determining the water of crystallisation in crystallised fluosilicates was tried (*Journ. Prakt. Chem.*, cii., 2). This method was to heat a weighed amount of the material; e.g., $\text{CuSiF}_6 \cdot \text{XH}_2\text{O}$ with a weighed amount of magnesium oxide. The reaction is as follows:—



To a known weight of magnesium oxide in a platinum crucible was added a solution containing a known amount of fluosilicic acid, and the mixture was well stirred. The reaction should be—



and upon evaporating to dryness and heating to redness, there should remain (according to Stolba) only $3\text{MgF}_2 + \text{SiO}_2$. With the same weight of fluorine in the form of hydrofluoric acid only 3MgF_2 would remain according to the equation—



knowing the total amount of fluorine that in the form of hydrofluoric acid and of fluosilicic acid in a mixture could be calculated by the increase in weight of the magnesium oxide used. However, upon heating the mixture formed as in Equation (a) to a temperature somewhat below redness, the increase in weight was considerably more than required by theory, showing that all of the water had not been driven off. Upon increasing the heat until a low red was reached, there was a continued decrease until the loss in weight was much greater than that required to account for the loss of water. Therefore it was found that this method is of no use for distinguishing between hydrofluoric and fluosilicic acids, and its value in determining the water of crystallisation as given by Stolba is at least very doubtful.

For the determination of fluorine in soluble fluorides, Greef takes advantage of the fact that ferric chloride forms with sodium fluoride an insoluble complex fluoride, $\text{FeF}_3 \cdot 3\text{NaF}$, which does not give a red colour with potassium sulphocyanide (*Ber.*, 1913, xlvii., 251; see also Guyot, *Comptes Rendus*, 1870, lxxi., 274). By addition of a large amount of sodium chloride the complex fluoride is made sufficiently insoluble, and the end-point of the reaction is obtained by adding 5 cc. of a 5 per cent solution of potassium sulphocyanide and 20 cc. of a mixture of equal parts of alcohol and ether. When ferric chloride has been added in quantity sufficient to form the sodium-fluoride the next drop after vigorous shaking gives a pink colour to the alcohol ether layer. Knowing the concentration of the ferric chloride the amount of fluoride taking part in the reaction is readily calculated according to the equation $6\text{NaF} + \text{FeCl}_3 = \text{FeF}_3 \cdot 3\text{NaF} + 3\text{NaCl}$.

The results of this method are quite accurate provided that care is used in detecting the first permanent pink, that conditions of concentration of the different solutions

* From the *American Journal of Science*, xlii. No. 251.

are uniform, and that the solution of the fluoride as well as the ferric chloride standard be strictly neutral.

Since the presence of free acid causes a marked shifting of the end-point of this reaction, it was thought worth while to make a series of titrations, varying the amount of free hydrochloric acid in order to ascertain the effect on the quantity of ferric chloride necessary to give a permanent pink. Table IV. gives the results of these titrations.

TABLE IV.

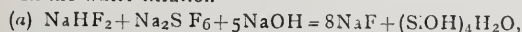
No.	NaF. Cc.	NaCl. Grm.	KSCu cc. 5 per cent	N. HCl. Cc.	FeCl ₃ solution. Cc.
1.	10	10	5	—	11.50
2.	10	10	5	—	11.55
3.	10	10	5	—	11.53
4.	10	10	5	0.1	11.11
5.	10	10	5	0.2	10.63
6.	10	10	5	0.4	10.10
7.	10	10	5	0.6	9.66
8.	10	10	5	0.8	8.88
9.	10	10	5	1.0	8.39
10.	10	10	5	2.0	5.90
11.	10	10	5	4.0	3.45 (?)
12.	10	10	5	1 (a)	11.65
13.	10	10	5	5	11.50
14.	20	20	10	—	23.12
15.	20	20	10	—	23.14

(a) Then neutralised.

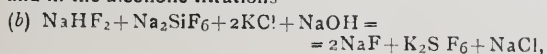
From the results as shown in this table it can be seen that very small amounts of free acid causes a relatively large decrease in the quantity of ferric chloride solution required. Thus in a volume of approximately 15 cc. only 0.1 cc. of normal hydrochloric acid causes a decrease of nearly 4 per cent in the result, while as much as 2 cc. causes a difference of almost 50 per cent. In Nos. 12 and 13 a small amount of acid was added, and then the solution was neutralised before titration just to ascertain how accurate the determination could be made when the solution was acid to begin with. The results show that with proper care a solution of alkali fluoride can be obtained nearly enough neutral to give quite an accurate determination.

Greef claims that by the use of the ferric chloride method he can estimate the amount of sodium hydrogen fluoride which is present in a mixture containing sodium fluosilicate. Greef's directions for this determination are as follows:—"Titrate a weighed portion of the mixture in hot water solution with standard sodium hydroxide using phenolphthalein as indicator. In this now neutral solution determine the total fluorine by titration with standard ferric chloride solution as described above. Dissolve another portion of the mixture in a small volume of water, and, after addition of alcohol until the concentration is approximately 50 per cent in alcohol, add about 1 grm. of potassium chloride, and titrate with the standard sodium hydroxide until neutral to phenolphthalein." In calculating the results from data obtained by following the above directions Greef assumes that the alkali used in the alcoholic titration is a measure of the total free hydrofluoric acid in the mixture, and that in the water titration for each equivalent of sodium hydrogen fluoride one equivalent of alkali is required, while for each equivalent of sodium fluosilicate four equivalents of the alkali are used. From the total fluorine as found by the ferric chloride titration, and from the results obtained in the water and in the alcohol titration, Greef calculates the content of the original material in sodium fluosilicate, sodium fluoride, and sodium hydrogen fluoride according to the following equations:—

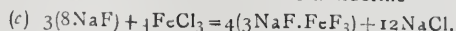
In the water titration—



and in the alcoholic titrations—



and the ferric chloride titration for total fluorine—



If there were no complications it is easily seen that the alkali used in Equation (b) would be equivalent to the sodium hydrogen fluoride present, while that used in (a) less that used in (b) would be a measure of the sodium fluosilicate present.

However, as has been shown by Katz (*Chem. Zeit.*, 1904, xxviii, 356), and also in the present paper, when a mixture of free hydrofluoric acid and of fluosilicic acid or sodium fluosilicate is titrated in alcoholic potassium chloride solution, a marked absorption of free acid takes place. On this account the titration as in (b) cannot be a measure of all the sodium hydrogen fluoride present in such a mixture as that described by Greef.

A NEW METHOD FOR THE DETERMINATION OF VANILLIN IN VANILLA EXTRACT.

By ARTHUR W. DOX and G. P. PLAISANCE.

THE official method for the determination of vanillin in vanilla extract consists essentially in removing the alcohol, extracting the vanillin with ether, crystallising it from the ethereal solution, and weighing it directly, identifying the crystals if necessary by their melting point. This method was first proposed by Hess and Prescott (*Journ. Am. Chem. Soc.*, 1899, xxi, 256, 719).

Modifications were subsequently introduced by Winton and Silverman (*Journ. Am. Chem. Soc.*, 1902, xxiv, 1128), and by Winton and Bailey (*Ibid.*, 1905, xxvii, 719).

For details of manipulation reference should be made to the official methods of the A.O.A.C. (*U.S. Bureau Chem.*, Bull. No. 152, p. 146).

The whole operation is rather lengthy and tedious.

Methods dependent upon the precipitation of vanillin by various reagents have been suggested but have not come into common use. Hanus (*Zeit. Untes. Nahr. Genussm.*, 1905, x., 585) used *m*-nitrobenzoylhydrazide as a precipitant, and also platinum chloride for estimating vanillin in the presence of piperonal (*Ibid.*, 1900, x., 657). Moulin (*Bull. Soc. Chim.*, 1903, xxix., 278) converted the vanillin into a yellow methyl picrate and estimated it colorimetrically. More recently Folin and Denis (*Journ. Ind. Eng. Chem.*, 1912, iv., 670) have devised a colorimetric method based upon the colour obtained by means of phosphotungstic and phosphomolybdic acids.

The writers have found that thiobarbituric acid in the presence of 12 per cent hydrochloric acid is a general reagent for the precipitation of aromatic aldehydes and have applied it to the quantitative determination of furfural (Dox and Plaisance, *Journ. Am. Chem. Soc.*, 1916, xxxviii., 2156, 2164). Under these conditions vanillin gave with thiobarbituric acid an insoluble vermilion coloured precipitate, which analysis showed to contain the percentages of nitrogen and sulphur required for the simple condensation product, 3-methoxy-4-hydroxybenzaldehydylthiourea. Since the reaction appeared to be practically quantitative, we decided to test out its possible application as a means of quantitatively estimating vanillin.

The first experiments were conducted with a standard solution of pure vanillin. Aliquots of this solution were precipitated with thiobarbituric acid in the presence of 12 per cent hydrochloric acid. The total volume of the reaction mixture was 50 cc. The precipitates were allowed to stand over night, then filtered on Gooch crucibles, washed with 50 cc. 12 per cent hydrochloric acid in small portions and finally with 20 cc. of water. The results are set forth in Table I.

In each case the filtrate was a lemon-yellow colour, indicating that a small amount of the condensation product remained in solution. This observation is further substantiated by the fact that the vanillin recovered

somewhat less than the amount taken. The error is, however, quite uniform, regardless of the amount of vanillin taken, averaging 2.6 mgrm. of the condensation product or 1.4 mgrm. vanillin. It is apparent, therefore, that a solubility correction must be applied just as in the determination of furfural by the official phloroglucinol method.

TABLE I.

Vanillin taken (grm.).	Weight of precipitate (grm.).	Vanillin recovered.	Error (mgrm.).
0.0200	0.0330	0.0180	-2.0
0.0200	0.0337	0.0184	-1.6
0.0200	0.0336	0.0184	-1.6
0.0200	0.0330	0.0180	-2.0
0.0500	0.0877	0.0480	-2.0
0.0500	0.0890	0.0487	-1.3
0.0500	0.0885	0.0484	-1.6
0.0500	0.0890	0.0487	-1.3
0.0500	0.0888	0.0486	-1.4
0.0500	0.0906	0.0495	-0.5
0.0500	0.0900	0.0492	-0.8
0.0500 (a)	0.0890	0.0487	-1.3
0.0500 (a)	0.0890	0.0487	-1.3

(a) Clarified with lead acetate.

Before applying the method to the determination of vanillin in commercial vanilla extracts, where clarification is necessary, the use of lead acetate as a clarifying agent was tested. In the last two determinations in the above table, lead acetate was added and the excess removed from the filtrate by hydrochloric acid before adding thiobarbituric acid. The results are in close agreement with the other results, showing that the small amount of lead chloride remaining in solution does not interfere with the determination.

A sample of vanilla extract of known purity was next used. The procedure was as follows:—25 cc. of the extract were dealcoholised in the usual manner, then transferred to a 50 cc. standard sugar flask and filled to the mark with lead acetate solution. After standing for several hours at about 37° C. the contents of the flask were filtered through a dry filter. The filtrate was a straw colour, indicating the absence of caramel as added colouring matter. 40 cc. of this filtrate was then transferred to another 50 cc. flask. Sufficient concentrated hydrochloric acid was added to bring the volume to 50 cc. and the acidity to 12 per cent. After standing a few minutes the lead chloride was removed by filtration through a dry filter and 40 cc. of the filtrate taken for the determination. On adding thiobarbituric acid in 12 per cent hydrochloric acid solution, an orange coloured precipitate resulted, indistinguishable in colour from the product with pure vanillin. However, the colour of the filtrate was somewhat darker than with vanillin alone, due no doubt to the original colour of the filtrate after clarification. The precipitate was allowed to stand over night filtered on a Gooch crucible, washed with hydrochloric acid and water as in the previous determination, and dried at 98°. The results are given in Table II.

TABLE II.

Vanillin extract taken, cc.	Aliquot per cent of extract taken.	Weight of precipitate, grms.	Weight of precipitate corrected for solubility.	Vanillin found in aliquot.	Vanillin in 25 cc. in extract, grms.	Vanillin in extract, per cent.
25	64	0.0450	0.0476	0.0260	0.0406	0.16
25	64	0.0450	0.0476	0.0260	0.0406	0.16
25	72	0.0501	0.0527	0.0288	0.0400	0.16
25	72	0.0498	0.0523	0.0286	0.0397	0.16
25	72	0.0510	0.0536	0.0293	0.0407	0.16
25	72	0.0501	0.0527	0.0288	0.0400	0.16
25	72	0.0502	0.0528	0.0289	0.0401	0.16
25 (a)	80	0.0890	0.0916	0.0501	0.0626	0.25
25 (a)	80	0.0882	0.0908	0.0496	0.0621	0.25

(a) Not clarified.

The above method is not applicable to artificial extracts where caramel is added as a colouring matter, since caramel contains furfural derivatives which react with thiobarbituric acid. The absence of caramel should first be demonstrated qualitatively. When caramel is present, the filtrate after clarification is brown instead of straw-coloured. A still more delicate test, described here for the first time, is the reaction with phloroglucinol. After clarifying and removing the excess of lead as chloride, phloroglucinol is added. In the presence of caramel a brown precipitate is formed. If caramel is absent, the vanillin gives a delicate rose pink colour or a slight pink precipitate. Clarification of the sample is necessary, as shown by the fact that the two determinations without clarification gave high results.

Thiobarbituric acid, which is easily prepared from malonic ester and thiourea, may be used for the quantitative determination of vanillin in vanilla extracts which do not contain caramel as added colouring matter. When caramel is present it may easily be detected by the brown precipitate formed on the addition of phloroglucinol to the clarified extract containing 12 per cent hydrochloric acid.—*American Journal of Pharmacy.*

DETECTION OF NICKEL IN COBALT SALTS.

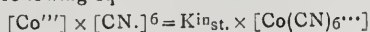
By A. R. MIDDLETON and H. L. MILLER.

THE use of dimethylglyoxime as a reagent for the detection and determination of nickel, discovered by Tschugaev in 1905 (*Ber.*, 1905, xxxviii., 2520), and developed by Brunk (*Zett. Angew. Chem.*, 1907, xx., 3444), has become quite general. In addition to its simplicity of manipulation and freedom from interference by other metallic ions this reagent is unusually delicate. The brilliant scarlet colour and extreme insolubility of nickel glyoxime (the nomenclature of Tschugaev, *Zeit. Anorg. Chem.*, 1905, xlv., 147) permits detection of one part of nickel in at least 350,000 parts of water, and a modified method of using the reagent will be described in this paper by which we have been able to detect one part of nickel in more than 4,000,000 parts of water.

For detection of traces of nickel in cobalt salts this reagent has not proved entirely satisfactory (*cf.* E. F. Smith, *Trans. Am. Electrochem. Soc.*, 1915, xxvii., 31). Cobalt combines with dimethylglyoxime to form an extremely soluble compound of brown colour. Either because the nickel salt is soluble in this compound or more probably because the cobalt appropriates most of the reagent, no nickel is precipitated by ordinary amounts of reagent from cobalt salt solutions even though a considerable amount is present. The object of this investigation was to devise a method by which the cobalt ion should be suppressed, thus permitting the reagent to react with nickel only, and avoiding the necessity for large amounts of reagent. Treadwell (*Analyt. Chem.*, i., 151, 7th ed.), following a suggestion of Tschugaev, accomplishes this result by transforming the cobalt salt into a cobaltic ammine by concentrated ammonia and hydrogen peroxide before adding dimethylglyoxime. We shall show that this method is unsatisfactory and fails when much cobalt is present.

The most striking differences in the chemical behaviour of nickel and cobalt are (1) the greater susceptibility of the latter to oxidation to the trivalent condition, and (2) the greater stability of its complex ions, both positive and negative. Of the various complex ions formed by cobalt the most stable are the complex cyanides, that of trivalent cobalt being decidedly more stable than that of bivalent cobalt. Nickel forms complex cyanides of a different type, resembling those of bivalent copper, whereas the cobalt cyanides are analogous to the iron cyanides. In the classic method of Liebig (*Ann.*, 1848, lxx., 244; 1853, lxxxvii., 128) for detecting nickel in cobalt salts, the inferior stability of the nickelocyanide ion together with

the ready oxidisability of cobaltcyanide to cobaltcyanide has long been used to effect a separation. For a solution containing cobaltcyanide, nickelcyanide, and cyanide ions the following equilibria are involved:—



and—



The values of the instability constants are not accurately known, but it is certain that that of the cobaltcyanide ion is extremely small, and that of the nickelcyanide ion much larger. Any reduction of the concentration of the cyanide ion in the solution must result in decomposition of the nickelcyanide ion, and considerable increase of nickel ion concentration, while the much more stable cobaltcyanide ion is less affected. In Liebig's method as modified by Gaube (*Zeit. Analyt. Chem.*, 1866, v., 75) the cyanide ion is removed by oxidation with alkaline hypochlorite or hypobromite, the nickelous ion being simultaneously oxidised and precipitated as nickel hydroxide. This method is not altogether satisfactory because cobalt hydroxide is usually precipitated also, and the appearance of a brown precipitate is by no means certain proof of the presence of nickel.

Since nickel glyoxime is decomposed by the cyanide ion our problem was to remove the cyanide ion so gradually that the cobaltcyanide ion should remain practically unaffected. For this purpose we have made use of the great stability of complex silver cyanide ions, together with the small solubility of silver argenticyanide, $\text{Ag}[\text{Ag}(\text{CN})_2]$, 0.0004 grm. per litre at 20° (Bredig, *Zeit. Phys. Chem.*, 1903, xlvii., 602). For argenticyanide ion $[\text{Ag}] \times [\text{CN}]^2 = 10^{-21} \times [\text{Ag}(\text{CN})_2^-]$ (Bodländer, *Zeit. Anorg. Chem.*, 1904, xxxix., 227). The comparative insolubility of silver cobaltcyanide, accurate data for which are lacking, should also tend to prevent decomposition of the cobaltcyanide ion. If to a solution containing alkali salts of nickelcyanide, cobaltcyanide, and a small excess only of cyanide, dimethylglyoxime be added and then dilute silver nitrate solution gradually, precipitation of silver argenticyanide removes the cyanide ion and promotes decomposition of the nickelcyanide ion, increasing the concentration of the nickelous ion, while the cobaltcyanideion is precipitated as $\text{Ag}_3\text{Co}(\text{CN})_6$, or, if not precipitated, is but slightly decomposed. Comparatively little dimethylglyoxime should then be sufficient to precipitate the small amount of nickel present, in part at least. The experiments recorded below show that this modification yields very satisfactory results.

Experimental.

Solutions and Reagents.—Nickel sulphate solution from Kahlbaum's "Kobalt-frei" salt was standardised by electrolysis (0.05008 N and by precipitation and weighing as glyoxime 0.04968 M). Cobalt, if present, was in very small amount; we were unable to detect it with absolute certainty. Iron was found present, and the discrepancy in the electrolytic and precipitation values is probably due almost entirely to its presence. Its removal appeared unnecessary for our purpose. The more dilute solutions used in the work were prepared from this solution by accurate dilution.

Cobalt sulphate solution, approximately 0.1 M, was prepared by working up residues from cobalt ammine salts. Nickel was removed by dimethylglyoxime according to the method we have developed, and the solution as used gave no test for nickel. By electrolysis this solution was found to be 0.0921 M.

The other reagents used were potassium cyanide, 10 per cent solution; dimethylglyoxime, 1 per cent solution in alcohol; and silver nitrate, 1 per cent solution.

Sensitivity of Dimethylglyoxime as Reagent for Nickel in Absence and in Presence of Silver Cyanide.—Two 10 cc. portions of each of the NiSO_4 solutions of the concentrations stated in Table I. were taken. One was warmed to about 80°, 1 cc. of the dimethylglyoxime reagent added,

and a drop or two of dilute ammonia. The other portion was converted into the complex cyanide by adding two or three drops of KCN. At these small concentrations no precipitate of nickel cyanide was formed. The solution was warmed to 80°, 1 cc. of dimethylglyoxime reagent added, and then AgNO_3 solution dropwise until a permanent white or pink precipitate formed. The more concentrated solutions thus treated gave at once pink precipitates; the more dilute ones white precipitates which turned pink on standing. In those solutions which required more than one hour to form a precipitate the exact time required for the pink colour to appear was not recorded. In these cases the samples were observed after standing twenty-four hours. In the extreme dilutions of the simple ion the precipitate was frequently a single red crystal, very minute and difficult to see.

TABLE I.

Molar conc.	NiSO_4 .	$\text{K}_2\text{Ni}(\text{CN})_4$.	Mg. Ni per cc.	Dilution.
0.0005	Immediate	Immediate	0.02934	1:0.034 × 10 ⁶
0.00005	1 hour	3 mins.	0.002934	1:0.34 × 10 ⁶
0.00001	24 hours	5 mins.	0.000587	1:1.7 × 10 ⁶
0.000009	24 hours	10 mins.	0.000528	1:1.9 × 10 ⁶
0.000008	24 hours	20 mins.	0.000470	1:2.13 × 10 ⁶
0.000007	24 hours	30 mins.	0.000411	1:2.43 × 10 ⁶
0.000006	24 hours	1 hour	0.000352	1:2.54 × 10 ⁶
0.000005	24 hours	24 hours	0.000293	1:3.4 × 10 ⁶
0.000004	No ppt.	24 hours	0.000235	1:4.26 × 10 ⁶
0.000003	No ppt.	No pink colour	0.000176	1:5.3 × 10 ⁶
0.000002	No ppt.	No pink colour	0.000117	

From the results tabulated in Table I. it appears that the proposed modification shortens considerably the time required for the precipitate of nickel glyoxime to become visible, and also makes possible the detection of somewhat smaller concentrations of the nickel ion. Apparently this is due to increased concentration of these ions by adsorption upon the precipitated silver cyanide. As evidence in favour of this view it may be noted that we found that precipitation of silver chloride in extremely dilute solutions of the nickel ion and dimethylglyoxime was equally effective in hastening formation of the pink nickel glyoxime, while precipitation of a positive colloid, such as aluminium hydroxide, had no effect whatever. Since both silver cyanide and silver cobaltcyanide are white, the red nickel glyoxime is readily seen as a pink tint in the white precipitate and the delicacy of the reagent is increased.

Oxidation of Cobaltcyanide to Cobaltcyanide.—When KCN is added to a solution of a cobalt salt, brownish white $\text{Co}(\text{CN})_2$ is precipitated and then redissolved to a greenish brown solution of $\text{K}_4\text{Co}(\text{CN})_6$. When warmed this changes soon to a pale yellow colour, and the colour change is frequently assumed in manuals of analysis to indicate completion of oxidation. When AgNO_3 was added soon after the colour change took place, we found that the solutions darkened and dark grey precipitates were formed, while solutions which had stood for several hours after cyanide was added did not darken, and gave pure white precipitates. When one of the darkened solutions became distinctly opalescent we inferred that some silver ion had been reduced by cobaltcyanide which was still present, according to the reaction $\text{K}_4\text{Co}(\text{CN})_6 + \text{AgNO}_3 = \text{K}_3\text{Co}(\text{CN})_6 + \text{Ag} + \text{KNO}_3$. By adding silver nitrate solution to freshly prepared solutions of cobaltcyanide we found that this reaction takes place very slowly in cold but rapidly in hot solutions. When the silver nitrate was added dropwise the hot solutions first became lighter in colour, then gradually turned orange, and darkened until a grey precipitate was formed. If the addition of silver nitrate was stopped when the orange tint appeared no precipitate formed, but the solution darkened on standing and became opalescent due to the formation of colloidal silver. This reaction was found to be regularly reproducible in solutions of cobaltcyanide not less than 0.005 M.

We next investigated the time required after the colour change to complete the oxidation, taking the failure to form metallic silver as evidence that oxidation was essentially complete. Ten cc. portions of 0.1 M CoSO_4 were treated in casseroles with just enough KCN to dissolve the precipitates, heated nearly to boiling, and continuously rotated in the casseroles for a definite time to hasten oxidation. The solutions were diluted to 100 cc. with water at 85° , and silver nitrate was added dropwise with vigorous stirring. All solutions which had been warmed less than five minutes gave colloidal silver or dark precipitates; those heated for at least this period did not darken, and gave pure white precipitates. Presumably the time required increases with the amount of cobalt. Gauhe (*loc. cit.*) showed that the oxidation of cobaltocyanide requires considerable time, but his experiments appear to have been forgotten.

Detection of Silver in Cobalt Salts.—We next determined the minimum amount of nickel that could be detected in varying amounts of cobalt salts by our silver method, and, for comparison, by two of the older methods, Treadwell's and that of Liebig-Gauhe.

A. The Silver Method.—Definite volumes of solutions of NiSO_4 and CoSO_4 of known concentration were measured from burettes into a casserole, KCN was added until the precipitate just dissolved, and the solution heated and rotated for five minutes after the change of colour was noted. The solution was then diluted with water at 85° to 50 cc., 1 cc. of dimethylglyoxime solution was added, and then silver nitrate dropwise with constant stirring until a permanent precipitate was produced. The time required for the pink colour of nickel glyoximine to appear was observed. In cases where the time exceeded one hour observations were made at the end of twenty-four hours. The results appear in Table II.

TABLE II.

NiSO_4		Ni mgrm.	Ratio Ni:Co.	Ratio Ni: H_2O . Approx.	Results. Pink precipitate in—
Vol. cc.	Molar concn.				
2.0	0.0005	0.0587	1:925	$1:0.85 \times 10^6$	Immediate
1.5	0.0005	0.0440	1:1234	$1:1.14 \times 10^6$	4 mins.
1.0	0.0005	0.0293	1:1851	$1:1.71 \times 10^6$	6 mins.
4.5	0.0001	0.0264	1:2054	$1:1.89 \times 10^6$	10 mins.
4.0	0.0001	0.0235	1:2314	—	20 mins.
3.5	0.0001	0.0205	1:2614	$1:2.44 \times 10^6$	30 mins.
3.0	0.0001	0.0176	1:3085	—	24 hours
2.5	0.0001	0.0137	1:3702	$1:3.65 \times 10^6$	24 hours

(In each experiment 10 cc. CoSO_4 0.0921 M, equivalent to 54.31 mgrms. Co was used).

Taking the minimum amount of nickel, 0.0205 mgrm., which could be detected in cobalt within thirty minutes, we studied the effect of larger proportions of cobalt. The procedure and final total volumes were the same as in the preceding experiments. The results are shown in Table III., and indicate that the sensitiveness of the test is not appreciably impaired by the presence of large amounts of cobalt.

TABLE III.

CoSO_4 0.0921 M cc.	Mg. Co.	Ratio Ni:Co.	Results.
15	81.47	1:3966	Precipitate pink 30 mins.
20	108.62	1:5288	
25	135.78	1:6610	
30	162.93	1:7932	

B. The Treadwell Method.—Ten cc. portions of 0.0921 M CoSO_4 , equivalent to 54.31 mgrms. Co, with varying small amounts of NiSO_4 were warmed with concentrated ammonia until a clear solution was obtained, hydrogen peroxide was added, and the solutions were heated till excess of peroxide and ammonia was removed, diluted to 50 cc., 1 cc. of dimethylglyoxime solution was added, and the time required for the precipitate of nickel glyoximine to appear was observed. The results are given in Table IV.

Taking the minimum amount of nickel that could be detected in one hour, 0.235 mgrm., the effect of larger

proportions of cobalt were studied. The procedure and final volume of solution were the same as in the experiments recorded in Table IV. The results are shown in Table V. Apparently this method is not very sensitive, and fails when much cobalt is present, at least with the small amount of dimethylglyoxime which was used.

TABLE IV.

NiSO_4		Mgrm. Ni.	Ratio Ni:Co.	Results.
Vol. cc.	Conc. molar.			
10	0.0005	0.293	1:185	Red precipitate 1 hr.
9	0.0005	0.264	1:206	
8	0.0005	0.235	1:231	
7	0.0005	0.205	1:264	Red precipitate 24 hrs.
5	0.0005	0.147	1:370	
4	0.0005	0.117	1:462	

TABLE V.

Cc. CoSO_4 0.0921 M.	Mgrms. Co.	Ratio Ni:Co.	Results
10	54.31	1:231	Red precipitate after 1 hr.
15	81.47	1:346	No precipitate after 1 hr.
20	108.62	1:462	

C. The Liebig-Gauhe Method.—Ten cc. portions of CoSO_4 0.0921 M, with varying amounts of NiSO_4 were treated with a slight excess of KCN over that required to dissolve the precipitate, and heated and rotated until complete oxidation of the cobaltocyanide had taken place. They were then diluted to 50 cc., and freshly prepared sodium hypobromite solution was added. After the precipitate had flocculated it was filtered off, washed, dissolved in dilute HCl, neutralised with ammonia, and tested for Ni with dimethylglyoxime.

TABLE VI.

NiSO_4 0.0005 M cc.		Mgrm. Ni.	Ratio N:Co.	Results.
Vol. cc.	Molar concn.			
9	0.0005	0.2641	1:206	Black precipitate Ni confirmed
6	0.0005	0.176	1:309	
3	0.0005	0.088	1:617	
2	0.0005	0.059	1:925	Black precipitate no Ni
1	0.0005	0.029	1:1850	
None	None	None	—	

This method appears able to detect 0.1 mgrm. nickel in a volume of 50 cc., but a confirmatory test must in every case be applied as the precipitate always contains cobaltic hydroxide if the hypobromite is added to a warm solution. Even if the temperature is kept low Co(OH)_2 frequently precipitates.

Comparing the results of the three methods the minimum amount of nickel detectable within one hour in a volume of 50 cc. is found to be:—

Silver method	0.02 mgrm.
Treadwell method	0.23 "
Liebig-Gauhe method	0.09 "

These figures do not adequately convey the relative merits of the three methods, for it should be noted that the Liebig-Gauhe method requires a confirmatory test to make the results quite reliable; the Treadwell method failed to show the stated minimum amount of nickel when so little as 231 times as much cobalt as nickel was present; while the silver method appears to retain its full sensitiveness in presence of any amount of cobalt; moreover, it increases the sensitiveness of dimethylglyoxime about eight times, and is able to detect within twenty-four hours less than 0.002 mgrm. of nickel in a volume of 50 cc.

Summary.

1. A modified method of using dimethylglyoxime for detecting traces of nickel in cobalt salts is proposed which (a) avoids the use of large amounts of this rather costly reagent; (b) makes possible the detection of considerably smaller quantities of nickel than has been possible heretofore.

2. The sensitiveness of the test is shown to be unaffected by the presence of cobalt even in large quantities. The proposed method increases the ordinary sensitiveness of dimethylglyoxime about eight times, and is capable of detecting about one-fifth the amount of nickel detectable by any of the previously known methods.—*Journal of the American Chemical Society*, xxxvii., No. 9.

THE PROTECTION OF THE MILK SUPPLY.*

By WILLIAM G. SAVAGE, M.D.
County Medical Officer of Health for Somerset.

THE four separate ways in which milk may be responsible for disease or ill-health. Each must be separately considered.

Chemical Impoverishment.—The existing chemical standards and how far they effect their object. Suggested alterations.

Tuberculosis spread by Milk.—The extent of the evil and its importance. The double nature of the problem—the elimination of bovine tuberculosis and the prevention of human tuberculosis from infected milk. Critical consideration as to how far the Milk and Dairies Act, 1914, and the Tuberculosis Regulations if re-enacted will give effective control.

The Conditions Necessary for Success.

Acute Infectious Diseases spread by Milk.—The diseases spread by milk. The additional control under the Milk and Dairies Act, 1914, and the necessary additions.

General Bacterial Contamination and the Production of Clean Milk.—The essentials of the problem. Why existing conditions are so unsatisfactory. The lines of reform. The position of bacteriological examinations in ensuring cleanliness. Value compared with systematic sanitary inspections. Existing arrangements for distribution and the substitution of active participation by the Local Urban Authorities. The effect of efficient milk control upon the quantity and price of milk. The importance of distinguishing between cost of production and cost of supervision. A large share of the latter should be from Treasury funds. If this is done the cost of production should not be materially increased. The extent to which improvements in the protection of the milk supply can be effected during the war and the steps which should be introduced after peace has been re-established.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, February 15, 1917.

Sir J. J. THOMSON, O.M., President, in the Chair.

PAPERS were read as follows:—

"On the Structure and Development of the Tubular Enamel of the Sparidae and Labridae." By J. H. MUMMERY, D.Sc.

The author endeavours to show that the enamel of sparidae and labridae is a true tubular structure. Stains can be made to enter the tubes and traverse their finest branches. The molar teeth of the sargus, which lie beneath the teeth in wear and are about to be erupted, show a very copious staining of the enamel over large areas, which in teeth further advanced to eruption become contracted until the narrow tubes characteristic of the functional tooth only are seen. This suggests a calcifying

function of the tubes, which show rows of granules in many places. The continuation of the calcifying process is rendered possible by the attachment of a pellicle of the enamel organ to the surface, which at the margins is in communication with the circulating blood, and a study of the developing teeth shows that there is a regular arrangement of blood vessels within the enamel organ.

The first portion of enamel laid down is formed by ameloblast cells, but in the later stages, as shown by C. Tomes in the Gadidae, the ameloblasts disappear and a stroma takes their place. The author has shown that the tubes in this stroma lie alternate to the blood vessels, which are enclosed in sheaths, and processes connect them with one another, enclosing spaces or alveoli between them containing small nuclei and granules, the whole evidently forming a secreting organ.

In the labridae the conversion of the enamel organ into a true secreting organ is still more evident, for in the American black fish (*Tautoga*) true tubular glands are seen surrounding the tubes containing the blood vessels, and ducts pass from them into the delicate stroma in which the enamel is being calcified.

The existence of a regular system of vascular tubes and of true glandular structures in these fish lends strong confirmation to the view of the secretory nature of enamel formation generally, combined, however, with the conversion of a portion of the cells of the enamel organ into the organic matrix of the calcified tissue.

"The Distribution in Wheat, Rice, and Maize Grains of the Substance the Deficiency of which in a Diet causes Polyneuritis in Birds and Beri-Beri in Man." By HARRIETTE CHICK and E. M. M. HUME.

"The Effect of Exposure to Temperature at or above 100° C. upon the Substance (Vitamine) whose Deficiency in a Diet causes Polyneuritis in Birds and Beri-Beri in Man." By HARRIETTE CHICK and E. M. M. HUME.

SOCIETY OF GLASS TECHNOLOGY.

Ordinary Meeting, February 15, 1917.

W. F. J. WOOD, B.Sc., President, in the Chair.

PREVIOUS to the meeting several series of glasses made from British sands were exhibited by Mr. C. J. PEDDLE, M.Sc., F.C.S. The effect of washing and grading was amply illustrated, and the fact that good colourless glass can be made from certain British sands after proper treatment was well brought out. Alongside the glasses were specimens of the various sands before and after treatment. The value of the exhibit was enhanced by a splendid set of micro-photographs, the work of Mr. Wilfred R. Barker, showing the grading of sands and illustrating the value of washing.

The following papers were read:—

"The Annealing of Glass." By F. TWYMAN.

The author pointed out that want of annealing in glass leading to fracture was due to the presence of internal stress. Glass behaves at all temperatures as a viscous liquid, and exhibits a continuous and gradual variation in viscosity from almost zero at high temperatures to almost infinity at 0° C. In molten glass there is no permanent internal stress, whilst at ordinary temperatures glass is almost perfectly elastic so that stress cannot originate at either high or low temperatures. At high temperatures internal stresses, if any, die away very quickly, but between this high temperature and the low temperature, where glass acts as an elastic solid, there is a region where internal stress may take several minutes or even hours to die away. It is this region of temperature which is important in annealing, and care must be exercised in cooling a glass object through its "annealing range" in order to free it from internal stress.

The author described the method employed to determine

* Abstract of Lecture delivered at the Royal Institute of Public Health, on February 28, 1917.

the annealing temperature of various glasses, and then showed that the mobility (*i.e.*, inverse viscosity) of glass doubled for each 8° C. rise in temperature. For temperatures near the annealing temperature of glass the following formula has been proved correct:—

$$M = k \times 2^{\left(\frac{\theta}{8}\right)}$$

where M is the mobility, *k* is a constant, and θ the temperature in °C.

Results were given showing the rapid rise of mobility with rise of temperature. Thus, a certain glass kept at 420° C. required a period of eighty-three hours for internal stress to disappear, whilst at 580° C. the same glass was freed from stress in 0.3 second. The actual annealing temperature, *i.e.*, the temperature at which stress easily disappears and yet low enough not to cause deformation of the object, differs widely for various glasses. It is a matter of wide importance to the manufacturer to know the annealing temperature of his glass. For example, suppose the annealing temperature of a glass is 500° C., *i.e.*, stress will almost disappear from the glass at this temperature in about three minutes, then if the glass is held at 420° C. it would require forty-five hours to anneal, whilst if kept at 580° C. it would probably go out of shape.

Considerable discussion ensued, the relative value of long and short lehrs, and the possibility of annealing different glasses at the same time being touched upon in particular.

"Annealing." By S. ENGLISH.

The demand from manufacturers as to improvements in processes of annealing, coupled with anomalous results obtained for the coefficient of thermal expansion of glass which was known to be strained had led to an investigation on annealing. In the first place some knowledge of the rate of annealing at various temperatures was sought, and with this end in view small glass rods were heated at the required temperature in an electric furnace, observations being carried out by means of a special apparatus built up of two Nicol prisms and a system of lenses. The well-known rings and cross as seen in an uniaxial crystal were always observed in the rod under experiment, and as the experiment proceeded the rings expanded and passed from the circle of light, the rate at which they disappeared being a measure of the rate of annealing at that temperature. Several lantern slides were shown illustrating the appearance of the rod as annealing proceeded, and results were given for several glasses. For example, the times necessary for the last four rings to disappear in the case of a chemical resistant glass were for various temperatures as follows:—

Temperature (°C.).	Time (mins.).
500	1230
550	50
600	20
625	12

The times required for the field of view in the apparatus to become perfectly dark, *i.e.*, until all stress had disappeared, were:—

Temperature (°C.).	Time (mins.).
550	570
600	270
625	18
650	10

Since the annealing of glass is the relieving due to incipient softening of internal strains the temperature at which annealing proceeds at a fairly rapid rate may be obtained by finding temperature at which glass will yield to external forces. The apparatus for carrying out this work was described, and curves were given showing results with actual glasses.

The optical and mechanical methods of determining annealing temperatures as described by the author, yield

results in close agreement, and prove that the annealing temperature of glass is considerably below the temperature of actual softening.

The next meeting of the Society will be held in Birmingham on Thursday, March 15, at 2 p.m., when papers will be read on the question of the construction of glass furnaces.

THE INSTITUTE OF METALS.

THE Annual General Meeting of the Institute of Metals will be held in the rooms of the Chemical Society, Burlington House, Piccadilly, W., on Wednesday and Thursday, March 21 and 22, 1917. The Meeting will commence at 8 p.m. on the 21st and at 4.30 p.m. on the 22nd, concluding the same evening. A special feature of the meeting will be a "General Discussion on Metal Melting." The following is the programme of proceedings:—

Wednesday, March 21 (at 8 p.m.).

General Meeting of Members in the Lecture Hall of the Chemical Society.

The Report of the Council on the work of the past year will be presented by the Chairman.

The Honorary Treasurer, Mr. A. E. Seaton, will present his report.

The results of the Ballots for the Council for 1917 and for the election of new Members will be declared.

The following communications will be read in abstract and discussed:—

"General Properties of Stampings and Chill Castings in Brass of Approximately 60/40 Composition." By Owen W. Ellis, B.Sc. (London).

"Machining Properties of Brass." By Owen W. Ellis, B.Sc. (London).

"Surface Tension and Cohesion in Metals and Alloys." By Sidney W. Smith, B.Sc., A.R.S.M. (London).

"Aluminium Production by Electrolysis: A Note on the Mechanism of the Reaction." By R. Seligman, Ph.D. (London).

"Annealing of Nickel Silver" (Part II.) By F. C. Thompson, D.Met., B.Sc. (Sheffield).

Thursday, March 22 (at 4.30 p.m.).

General Meeting of Members in the Lecture Hall of the Chemical Society. "General Discussion on Metal Melting."

The following communications will be read in abstract and discussed:—

"Metal Melting as Practised at the Royal Mint." By W. J. Hocking (London).

"Coal Gas as a Fuel for the Melting of Non-ferrous Alloys." By G. B. Brook (Sheffield).

"High Pressure Gas Melting." By C. M. Walter, M.Sc. (Birmingham).

"Contribution to Metal Melting Discussion." By H. M. Thornton (London) and H. Hartley, M.Sc. (London).

"An Electric Resistance Furnace for Melting in Crucibles." By H. C. Greenwood, D.Sc. (London), and R. S. Hutton, D.Sc. (Sheffield).

"Ideals and Limitations in the Melting of Non-ferrous Metals." By Carl Hering (Pa., U.S.A.).

"Metal Melting in a Simple Crude Oil Furnace." By H. S. Primrose (Ipswich).

Members intending to take part in the discussion of any of the above can be supplied with a copy a week before the meeting on application to the Secretary, subject to the operation of the regulations restricting the use of paper. Copies of the communications, it is hoped, will be available at the meeting for the use of members, and those who are unable to attend will subsequently be supplied, on application, with a copy of any communication of which prints remain.

In order that as much time as possible shall be available for discussion, communications will be read in abstract only, ten minutes being allowed to the author for that purpose, unless otherwise decided by the Chairman. Each speaker will be limited to five minutes in the discussion, unless the time should be extended by the Chairman. Speakers who are unable to give more than a summary of their views in the time available may send a written statement to the Secretary for publication in the June issue of the *Journal*. Such statement must be in the hands of the Secretary not later than noon on April 21, 1917.

New Offices.—The attention of members is particularly called to the fact that the address of the Institute has been changed to 36, Victoria Street, London, S.W., on account of Caxton House having been commandeered by the War Office. The telephone number remains unchanged. The new offices are more extensive and quieter than those vacated. In view of the increased rental of the new offices the Council feel that it is very desirable that there should be a speedy increase in the membership. It is hoped, therefore, that members will do their utmost to secure new members, in connection with the election of whom a meeting of the Council will be held on March 14.

All Membership applications that are found to be in order will be included in the ballot papers to be issued to Members on March 15, and the result of the ballot will be declared at the London Meeting on March 21.

All Candidates for Membership whose forms are in the Secretary's hands before March 14 will be entitled to take part in the Proceedings at the London Meeting.

A special membership booklet, which has been prepared by the Council as a suitable means for introducing the work of the Institute to those who are eligible for membership, will be forwarded with pleasure, on application being made to the Secretary. The booklet contains a considerable amount of information regarding the Institute, as well as a Membership Application Form.

A Membership Form will also be found at the end of the forthcoming volume of the *Journal* (Vol. XVI.), which will be issued to Members early in March. (A similar Form appears at the end of Vol. XIV.).

It might be pointed out to possible Members that their first subscription carries with it Membership until June 30, 1918.

May Lecture.—The Seventh Annual May Lecture will be given at the Institution of Civil Engineers, Great George Street, Westminster, S.W., on Thursday, May 3, 1917, at 8.30 p.m., by Prof. W. E. Dalby, M.A., F.R.S., on "Researches made possible by the Autographic Load-Extension Optical Indicator."

NOTICES OF BOOKS.

Elementary Qualitative Analysis. By BENTON DALES, Ph.D., and OSCAR LEONARD BARNEY, Ph.D. New York: John Wiley and Sons, Inc. London: Chapman and Hall, Ltd. 1916. Pp. vii+205. Price 5s. 6d. net.

This addition to the many books which are to be procured on the subject of elementary qualitative analysis presents some useful features, while showing no marked novelty or originality. The usual tests for common acids and bases are described, and schemes are given for the identification of unknowns, with some hints for shortening work by short cuts and incidental observations, the student being trained to think for himself and to work intelligently. On the whole, the experimental details are sufficiently full, although an exception must be made to this statement in the case of the examination of the emission spectra of substances, about which very scanty information is given. The questions on typical separations and miscellaneous

reactions given at the ends of the chapters are often of a very useful nature, and to answer them satisfactorily the student would frequently have to exercise a good deal of ingenuity.

Decennial Index of the Analyst. Vols. XXXI.-XL. (1906-1915). Compiled by MURIEL A. BAKER. London: Simpkin, Marshall, Hamilton, Kent, and Co., Ltd. Pp. 732.

THE preparation of the "Decennial Index of the Analyst for 1906-1915" has just been brought to a conclusion, and the new volume in some ways differs widely from its predecessors. An alphabetical list of authors, with the titles of their communications, is first given, and then a full subjects index, which is so arranged that reference to it is as simple as possible, and it will be found quite easy to look up any communication, even if one's recollection of the title is very hazy. Thus such an article as "New Thermochemical Method for Sub-dividing Accurately a given Interval on the Thermometer Scale," to take an instance at random, is indexed under "Thermochemical Method," "Interval," "Thermometer Scale," and "Scale," besides, of course, appearing in the authors index. The last part of the book is a list under the authors' names of the papers read before, or directly communicated to, the Society of Public Analysts and other Analytical Chemists. The indexing appears to have been carefully done, as far as can be estimated from a somewhat cursory examination, and the new arrangement will undoubtedly be found satisfactory.

CORRESPONDENCE.

THE NEWSPAPERS PATRIOTIC TOBACCO FUND.

To the Editor of the Chemical News.

SIR,—The question in everyone's mind at the present moment is whether our fine fellows at the front are going to win through to victory in 1917. We all hope they are, and we at home must support them in every way we can.

The particular work which this Fund has taken upon itself is to supply our men on active service abroad with tobacco and cigarettes—comforts which are perhaps more appreciated than anything else.

We have already collected, with the valuable assistance of newspapers throughout the country, over £32,000, every penny of which has been spent on the purchase of smokes, and smokes alone.

But, unfortunately, cigarettes do not last long. Men at the front do not get anything like enough. Out there they need to smoke ever so much more than they did at home. A cigarette is their chief solace and comfort.

We are therefore making a further appeal—and we trust it will be a final one—to enable us to augment the very meagre supplies the men receive through the authorities.

Every shilling contributed to our fund sends about a week's supply to some brave fellow. The parcel contains 50 good cigarettes and a packet of splendid smoking tobacco, purchased at in bond duty-free prices. The parcels are taken to the front free of charge through the kind co-operation of the authorities.

A £5 donation will send a week's supply to 100 men, and a contributor can nominate the battalion and regiment which is to benefit. £50 will send a week's supply to every man in a battalion.

A pleasant feature of our plan is the enclosing in every shilling parcel of an acknowledgment postcard addressed back to the donor, thereby forming a link of friendship between the giver and each soldier.

These postcards are used by the men to thank the contributor direct, and, needless to say, are much appreciated, as they form a tangible proof of the good service which has been rendered by the contributor.

If any of your readers can spare something for our Fund I shall be most happy to acknowledge their contributions, however small, and assure them in advance of the heartfelt thanks of the British Tommies.—I am, &c.,

S. H. PHILLIPS, Hon. Secretary.

25, Haymarket, London, S.W.,
February 20, 1917.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

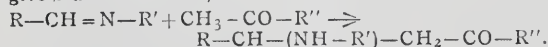
Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clxiii., No. 23, December 18, 1916.
This number contains no chemical matter.

No. 26, December 26, 1916.

Cristobalite.—Henri Le Chatelier.—The author has previously discovered the existence of a variety of silica X characterised by a point of transformation situated at 215°. This transformation is accompanied by an abrupt change of the linear dimensions amounting to 1 per cent. The author suggested that this variety of silica might be identical with cristobalite, and further researches have shown that this view is correct. He has detected cristobalite in various specimens of artificial silica.

Bulletin de la Société Chimique de France.
Vol. xix.-xx., No. 11, 1916.

Formation and Properties of β -Amino-ketones derived from Aromatic Imines.—Charles Mayer.—The author has already shown that the imines, by a reaction recalling aldolisation, combine with ketones to give β -amino-ketones,—



The aldehydes condense similarly, but subsequently undergo secondary reactions. The above reaction is not limited, as the author first thought, to methylated ketones. Thus an alcoholic solution of ethylphenylketone and benzylidene-aniline after a year deposited a crystalline mass from which the substance—

$C_6H_5-CH-(NH-C_6H_5)-CH(CH_3)-CO-C_6H_5$,
diphenyl-anilino-isopropyl ketone, could be isolated. In the case of certain compounds in which the CH_2 group is surrounded by two groups which give it an acid character, the condensation takes place similarly, but the compound formed then loses a molecule of primary amine to give the same compound as that obtained by the condensation of the aldehyde corresponding to the amine employed. Thus benzylidene-aniline reacts in alcoholic solution with cyanacetic ether to give ethyl benzylidene cyanacetate prepared by the usual methods. The β -anilino-ketones react with acetyl acetic ether to give a condensation product with elimination of aniline.

Chemical Society.—Fellows are notified that the lecture by Mr. Chaston Chapman, entitled "Some Main Lines of Advance in the Domain of Modern Analytical Chemistry," will be delivered on Thursday, March 15, 1917, at 8 p.m., instead of, as previously announced, on May 17. On the latter date, Dr. Horace T. Brown, F.R.S., will give his lecture on "The Principles of Diffusion—their Analogies and Applications."

MISCELLANEOUS.

"Chemical Engineering" and the Works Chemist.—The prospectus of the early volumes of this monthly journal shows that it is doing useful work in the scientific world in publishing articles of considerable interest in various branches of chemical technology. A very wide range of subjects is treated, and recent work appears to be well represented, while the list of subscribers includes the names of many of the most important firms of chemical manufacturers, engineers, &c.

The Chemical Directory of the United States.—This Directory, recently published by Messrs. Williams and Wilkins, of New York, Baltimore, and London, aims at giving comprehensive information relating to chemical and metallurgical equipment, chemicals, chemical supplies, new methods and appliances, and trade and professional journals, with a complete review of the advances in chemical technology made during the last two years. It is thus a useful addition to the library of the chemist and works manager, and all who are interested in the buying or selling of chemicals, apparatus, or machinery will find it a valuable possession.

MEETINGS FOR THE WEEK.

- MONDAY, 5th.—Royal Society of Arts, 4.30. (Aldred Lecture).
"Memorials and Monuments," by L. Weaver.
— Roy Institution, 5. (General Meeting).
— Society of Chemical Industry, 8. "Composition of Power Gases," by W. A. Tookey.
- TUESDAY, 6th.—Royal Institution, 3. "Internal Combustion Engines," by Prof. W. E. Dalby.
- WEDNESDAY, 7th.—Royal Society of Arts, 4.30. "German Business Methods," by J. H. Vickery.
— Society of Public Analysts, 8. "Quantitative Estimation of Mercury in Organic Compounds," by J. E. Marsh and O. G. Lye. "Composition of Milk," by P. S. Arup, H. C. Huish, and H. D. Richmond. "Studies in Steam Distillation—Part IV., Propionic, Butyric, Valeric, and Caproic Acids; Part V., Analysis of Acetic Anhydride and Alkyl-malonic Acids," by H. D. Richmond. "Salvarsan and Neo-salvarsan," by J. Webster.
- THURSDAY, 8th.—Royal Institution, 3. "Sponges—a Study in Evolutionary Biology," by Prof. A. Dendy.
— Royal Society. "Some Effects of Growth-promoting Substances (Auximones) on the Growth of *Lemna minor* in Culture Solutions," by W. B. Bottomley. "Some Effects of Growth-promoting Substances (Auximones) on the Soil Organisms concerned in the Nitrogen Cycle," by Florence A. Mockridge.
- FRIDAY, 9th.—Royal Institution, 5.30. "The Treatment of Wounds in War," by Sir Almroth Wright, C.B.
- SATURDAY, 10th.—Royal Institution, 3. "Imperial Eugenics—Saving the Soldier," by C. W. Saleeby.
— Ceramic Society, 7. "Necessity for the Application of Science and Art in Modern Pottery Manufacture," by J. Eyre. "Do Fireclays contain Halloysite or Clayite?" by J. W. Mellor.

Cloth, 3/6; Paper covers, 2/6. (Postage, 4d. extra).

THE WHEAT PROBLEM:

Based on Remarks made in the Presidential Address to the British Association at Bristol in 1898.

REVISED WITH AN ANSWER TO VARIOUS CRITICS

By SIR WILLIAM CROOKES, F.R.S.

SECOND EDITION.

WITH PREFACE AND ADDITIONAL CHAPTER, BRINGING THE STATISTICAL INFORMATION UP TO DATE.

With Two Chapters on the Future Wheat Supply of the United States, by Mr. C. Wood Davis, of Peotone, Kansas, and the Hon. JOHN HYDE, Chief Statistician to the Department of Agriculture, Washington.

CHEMICAL NEWS OFFICE,
16, NEWCASTLE ST., FARRINGDON ST., E.C.

THE CHEMICAL NEWS

VOL. CXV., No. 2989

SOME NATURAL WATERS OF CENTRAL NEW YORK.

By NICHOLAS KNIGHT.

THE little stream from which the city of Oneida, New York, receives its water supply, and also the reservoir, are located in the midst of the Salina shales. In some places these shales contain considerable quantities of gypsum, many times quite large masses of selenite.

The Soil Survey of Madison County, New York, issued by the Government Printing Office of Washington in 1907, contains an account of the geology of the region. It is there stated that the ravine occupied by the city reservoir is Upshar clay, the sides of the surrounding slope are Allis clay, and the higher portion of the watershed Miami stony loam. The Upshar clay is derived directly from the disintegration and weathering in place of the red Salina shales of the Silurian Age. The Allis clay is formed by the weathering in places of the light coloured Salina shales.

The Miami stony loam is derived from the weathering in place of a comparatively heavy mantle of glacial material deposited as a terminal moraine by one of the later advances of the ice-sheet at about the close of the glacial epoch in this section. It is not likely that the hard local limestones have contributed any considerable amount of material to the formation of the till, but that the soft red shales along the foot hills have contributed to it is evident from its colour. It is, however, quite probable that the limestone now contributes to the soil or soil solution.

The character of the soil in which the reservoir is located as well as that of the watershed itself accounts for the large amount of hardness in the form of calcium sulphate and calcium and magnesium carbonates. It is necessary to employ water softening plants in order to use the water in the manufacturing industries of the city, and also in the engine boilers of the different railway lines. The analysis of the water is given in Table I.

TABLE I.—Parts per Million.

Total solids	1029.0
CaSO ₄	561.3
CaCO ₃	305.8
MgCO ₃	134.5
Iron and alumina	1.6
SiO ₂	5.00
NaCl	20.0
CO ₂	91.5
Free ammonia	0.048
Albumenoid ammonia	0.072
Nitrates	0.34

While unusually hard the water shows rather unusual freedom from organic contamination.

The proposed supply for the city, the water from Florence Creek, is of a very different quality. It is about 20 miles north of the City of Oneida. The stream is 14 miles long, and the watershed averages one and a fourth miles in width, comprising an area of 17 square miles. In the locality of the stream the rainfall makes an average flow of one million gallons daily for each square mile of watershed, so the daily average would be seventeen millions of gallons.

The main reservoir to hold two hundred millions of gallons will be located at the hamlet of Glenmore, and if

necessary to meet the needs of the growing city another reservoir to hold five hundred millions of gallons can be constructed farther up the stream. The watershed is very sparsely settled, scarcely containing one residence per square mile, and the danger of contamination is accordingly very slight. The sides of the stream are steep and wooded, and the bed is rocky for the most part and the current is quite swift. An analysis of the water gave the results shown in Table II.

TABLE II.—Parts per Million.

Total solids	71.6
CaSO ₄	12.8
CaCO ₃	28.77
MgCO ₃	14.98
Fe ₂ O ₃	1.16
SiO ₂	2.20
NaCl	11.80
Free ammonia	0.04
Albumenoid ammonia	0.07
Nitrogen in nitrates	1.19
Nitrogen in nitrites	0.00
CO ₂	25.00

The water is unusually soft and is in marked contrast to the present supply. An analysis of the rock taken from the bed of the stream at the hamlet of Glenmore gave the results shown in Table III.

TABLE III.

	Per cent;
SiO ₂	79.94
Al ₂ O ₃	4.75
Fe ₂ O ₃	8.24
CaO	4.89
MgO	1.91
K ₂ O	0.04
Na ₂ O	0.00
Total	99.77

The rock is quite a pure sandstone with very little calcium and magnesium, which accounts for the softness of the water. It is a sandstone of the Medina formation, which at Glenmore borders closely on the Hudson River shales.

We desire to express our thanks to Mr. Vernon C. Shippee, Assistant in the Cornell College Chemical Department, for making the analysis of the rock.

Cornell College, Mount Vernon, Iowa,
February 6, 1917.

OUR ANALYTICAL CHEMISTRY AND ITS FUTURE.*

By W. F. HILLEBRAND, Ph.D.
Chief Chemist of the Bureau of Standards, Washington, U.S.A.

IN an address (*Journ. Am. Chem. Soc.*, 1905, xxvii., 300) read at Philadelphia nearly twelve years ago, I gave expression to some thoughts on the condition of analytical chemistry in our country as the condition appeared to me then to be. Those thoughts were based on an experience of many years, during which I was engaged wholly in analytical work of a more than ordinarily exacting nature, and especially upon observations that had been acquired in connection with several series of co-operative analyses of diverse materials. Since then my attention has been

* The Chandler Lecture, 1916, delivered before the Columbia University, U.S.A.

† To several of my colleagues in the Bureau of Standards, to whom the first draft of this address was submitted, I am under obligations for suggestions that have been most helpful in its further elaboration.

no less given to analysis, largely for the past eight years in a supervisory capacity however, and I have had opportunity to note the conditions that now prevail with respect to chemical analysis and what an important bearing exact analytical work often has on problems of physical and electro-chemistry, metallurgy, &c.

It seems to me, then, that I can choose no more fitting subject for my present discourse than a continuation of one so closely related to my life-work, one in which I feel a deep interest and of which I may be presumed to have knowledge somewhat worth presenting on an occasion like this. Then, too, since my remarks will apply most directly to analysis as it concerns the producers of the raw materials and the users of the products of applied science, the subject is eminently a proper one for the present occasion, and particularly so in an institution where applied chemistry made one of its important starts in this country, in the old School of Mines, with which the name of Chandler is so inseparably connected.

Although I shall cover now some of the ground traversed in my address of twelve years ago, in briefly alluding to the conditions of analytical chemistry in the present year, 1916, there is much to be said in developing one or two of the ideas then simmering in my mind and other phases of the general subject not then mentioned. So my subject calls for a more unrestricted title than I gave it at that time, and I shall speak to you of our analytical chemistry and its future, purposely restricting myself to a consideration of conditions as they exist and may become in this country.

In the early days of chemistry there was needed a vast accumulation of observations to serve as foundations for the development of the science. At the very basis lay the need for knowledge of the composition of all kinds of matter. Hence it came about that many, if not most, of the great chemists of the time were of necessity analysts, and the analytical branch of chemistry stood in high repute. That this condition did not maintain itself, that chemical analysis during the latter half of the past century fell from its high estate and came to be looked upon more or less as a handy tool for ulterior ends, a tool, moreover, which need not for most purposes be of the sharpest or the best, or entrusted only to the most careful and skilled operators—all this has been recognised and lamented by many. The reasons for the fall are also well enough known and need not be discussed at length, but brief reference to some of them will be needed in view of later remarks.

Chief among the reasons for the neglect of analytical chemistry is the enormous development, first of organic chemistry and later of the so-called physical chemistry. The effect was brought about in two ways:—(1) by mere displacement, as it were, owing to the far greater promise of new discoveries; however commonplace, or because of the strong interest attaching to new and unexplored fields of inquiry; (2) by the unfortunate fact that for a long period approximate analytical results were thought to suffice in most of the industries, and even in scientific researches. This meant that slipshod work and methods came more and more into use and less fundamental knowledge of analysis seemed to be demanded of chemists—all of which reacted unfavourably upon the standing of the analytical profession, tending to discredit it as a whole, even though it held members fit to rank with the illustrious pioneers.

In addition, some chemists came to feel that the field was an exhausted one, offering little to reward the research worker. How little this is true the events of recent years have abundantly shown. The growing sense of the important influence of small, even minute, amounts of this or that element or combination in a given material, and the high value of many ores and commercial products, has led to more critical examination of the methods used for determining the content of the substances in question in order to ascertain with greater precision the value of those materials, just as had been done long before for the

precious metals, gold and silver. Such examination revealed not infrequently unsuspected defects in methods regarded hitherto as reliable and accurate, and that good results were due often to compensation of errors or were to be had only within a narrow range of conditions. One good effect of such investigations has been to make conservative analysts distrustful of all new methods and less reliant on some of the old ones until their worth and suitability have been put to far more crucial test than was formerly deemed necessary.

Yet notwithstanding improvements made in important methods through painstaking research, it is evident that many methods will require a study differently directed or more profound than any yet made before light enough to meet even our immediate needs is thrown upon them. And who shall say what needs another century or even decade may bring forth? Are we not again and again even now confronted with the need to determine smaller and smaller amounts of a component and to make more and more perfect separations in order that the first may be possible? Are we to assume that a limit has been reached?

Another fact shows how untrue it is that the field of chemical analysis has little new to offer. Few ever thought, not so long ago, to look for the rarer elements in an ore or industrial product made from the ores. No use whatsoever was made of certain elements that are now serving most useful ends, either by themselves or in combinations. There are other elements, still chemical curiosities, for which no use has yet been found. Is there any more reason to believe for them than for the others that uses will never be found? Rare though they be, like gallium, indium, and germanium, and costly their extraction, the finding of a use for them will broaden the search for their ores and lessen the cost of production. With use will come a demand for methods of separation and determination, which must be accurate because of the small percentages in question or the enormous value of the material.

But there are other fields in which the chemist has to look to analysis of the highest order for help in solving his problems. For instance, the importance of exact analytical methods in connection with physico-chemical researches is very great and is, perhaps, best illustrated in the preparation of pure materials. There is no question that physical constants, even atomic weights, have been determined, not infrequently, upon materials of doubtful or at least unproved purity. The practice is all too common of assuming that a certain number of crystallisations or distillations is sure to yield a product of highest purity. Conclusive results can be obtained only when methods are devised and applied by which the amounts of any possible contaminant present can be proved to be without influence upon the results sought. A single instance, borrowed from the experience of the Bureau of Standards, may be of interest. In the preparation of pure alcohol to be used in the determination of a series of densities, tests were devised or confirmed for detecting the presence of minute amounts of ether, aldehyd, methyl alcohol, and water. The most delicate test for the latter was found to be the critical solution temperature of mixtures of kerosene and the alcohol to be tested. By this means the presence of 0.001 per cent of water in the alcohol could be readily detected.

In the field of electro chemistry there is a similar need for exact analytical data. In the determination of the electro-chemical equivalent of silver, from which the value of the ampère is derived, researches extending over several years have shown that the purity of the electrolyte is of fundamental importance. Thus, it was found that the presence in the electrolyte of the amount of organic matter derived from filter-paper by the passage through it of the distilled water used, was sufficient to cause an appreciable effect upon the structure and weight of the silver deposit. In this case delicate analytical procedures were devised for detecting minute amounts of such contaminants.

In the same research the study of the magnitude of possible occlusions in the silver deposits has involved the use of painstaking analytical methods at the Bureau and elsewhere.

Similarly, it is believed that the securing of accurate information regarding the operation of commercial baths for electro-deposition will depend largely upon the application of exact analytical methods. Thus, preliminary observations have shown that very slight differences in the neutrality of nickel baths may produce great effects upon their operation. Here the application of the hydrogen electrode as an analytical tool will probably be of service. The great number of empirical observations regarding the effect of addition agents in plating baths will become intelligible only when means are found and applied for determining quantitatively minute amounts of the addition agents (for instance, one part per million of glue) or of their decomposition products.

The application of some of the concepts of the modern theoretical chemistry has helped much to a better understanding of the limitations of some common methods, of how to reduce the errors of one or another of them within more or less acceptable bounds, and of why others are not open to improvement. The same principles applied to the development of new methods will, it is to be hoped, lead more quickly to success than in the past, by enabling the discoverer to take account from the start of earlier mistakes or omissions, and thus avoid the wasted effort that has been all too common.

At this point it may not be amiss to point out certain criticisms that apply to many new methods as first published. Almost no new method that has been prepared has been so vigorously worked out as to show all or nearly all of its limitations. Generally the start is with the presumably pure single substance, and the amounts operated upon are of considerable magnitude and do not cover a wide range of weights. This is not so serious a defect as to omit trying out a method that involves separations from other substances under a wide range of conditions as to relative and absolute amounts of the elements or compounds in question. A whole list is often given of results obtained in presence of other elements, but almost always the amount of the substance sought is considerable. No light is shed on the value of the method when that substance is in very small amount and the other greatly preponderates. Nor, in too many cases, is any proof afforded that results apparently good are really good and that more or less serious compensating errors are not involved. The consequence is often, as I have said, that one cannot take new methods at their face value or proceed to apply them under any and all conditions. They must first be more critically examined in order to complete and round out the work that was neglected. How this can be done will be discussed later.

What I have just said is not to be taken as necessarily reflecting upon the deviser of the incomplete method, nor need it deter others from trying to originate new methods or to improve old ones. There will be and must always be road-breakers and pioneer surveyors. Some fertile minds are fitted to make brilliant reconnaissances and unfitted for the laborious working in of details. Both types of chemical workers are needed. The former will still find ample opportunity for flights of invention and there will be no lack of room for the able and painstaking deliver into the depths.

In the address already alluded to and elsewhere I dwelt upon the unsatisfactory condition in which the art of analysis had been shown to be and expressed the conviction that our educational institutions must bear a large share of the blame in the matter. The faults which might be chargeable were perhaps more often those of omission than of commission, but I was able to point out no certain or even likely way which might lead to a better future. I think it may be worth while to reproduce certain paragraphs, with slight rearrangement, to serve not only as groundwork for what is to follow, but also as pos-

sibly suggestive leaders to those of you who are or expect to become analytical chemists or teachers of analytical chemistry.

"Many inquiries addressed to the participants in one series of analyses elicited the information that few knew anything definite about the quality of the water they were using, though examination showed it to be bad in a few instances and on the border line in others. Still less was known as to the quality of the reagents, except that they came from reputable firms. One admitted that a flaky sediment showed in his ammonia bottle, but he used only the clear liquid above. If the sediment represented silica from the bottle, as it may well have done, what had become of the other constituents of the attacked glass unless they were in solution?

"Now why were these things possible unless because it had never been sufficiently impressed upon the analysts in their student days that without proper tools to work with, among which water and reagents are first to be considered, good work is impossible? You doubtless do not fail rightly to tell them that absolute accuracy is unattainable in analysis, but do you make it plain that approximation is possible and that it will be the closer the greater the care bestowed upon the tools and at every step of the analysis itself? Is a student ever required to find out by actual test how good his water is, and both the kind and amount of its contamination, if such there be? Is it customary to instruct him in the testing of his reagents and as to the character of the contaminations to be looked for in all of the more important ones, or is he allowed to go forth with the impression that the label C. P., while not a flawless title, is a sufficient guarantee for all the demands of technical analysis? Is he, in fact, ever cautioned to find out, by actual test, the errors with which his work may be affected, due to imperfections in his tools of the kind just mentioned? And that without such knowledge and the ability to make correction for the defects, or the courage to fight for better materials with which to do, he will occupy a false position with respect to himself, his employers, and the community at large?

"Is the student's work ever checked against material of which the exact composition is known? I do not refer here to such things as simple salts, but to more complex bodies like limestone, cement, zinc ore or slag, in which many separations have to be made and all constituents should be determined. Is the student in such analyses religiously required to test the purity of his precipitates and the completeness of his precipitations by a careful examination of the filtrates? And is he taught that a satisfactory summation does not imply correct separations? Or that closely agreeing duplicates are not proof of good work?

"Only by such exercises can the young worker gain any knowledge as to his own power to do good work, and acquire that proper confidence in himself which is so essential.

"My experience of the past few years has convinced me that in these respects, at least, much is neglected that should not be neglected in the curricula of our colleges. It seems to me that if instruction in such fundamental essentials is not thoroughly drilled into the budding chemist, so that it becomes for him as much a matter of course afterwards to look to the quality of his tools as it is to weigh out his sample before analysing it, he has received a scant equivalent for his years of study, and that he has good grounds of complaint against his alma mater if he comes to grief by reason of her neglect."

To the foregoing reasons for poor results may be added the youthfulness and inexperience of most of the instructors in quantitative as well as qualitative analysis. There must be young instructors, of course, but one of the rules which should hold for the young child in the Kindergarten or Montessori school ought to hold here too, namely, that the work should be led by or at least most closely controlled

by one of experience and authority and of sympathetic insight.

If the conditions which I have sketched were true twelve years ago the question will be asked, and quite naturally: Have they improved? Candour compels me to say that evidences of improvement are few. In certain lines of work there has been some bettering of conditions, but we are still confronted with wide divergences in almost every direction between the results obtained by different analysts upon the same sample. I have many opportunities to note this fact in the co-operative work which is done upon the samples which the Bureau of Standards issues as standards for checking the skill of analysts or the value of methods used in industrial laboratories and educational institutions. The fact is further emphasised by the numerous requests received at the Bureau for umpire assays to settle the differences between commercial analysts, and still further by the comparative lack of sound or comprehensive knowledge of analysis among the young men who come to us from the colleges and universities.

(To be continued).

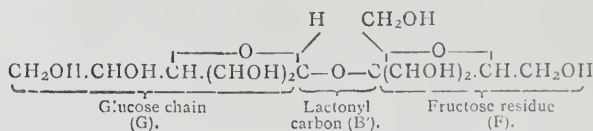
SOME NUMERICAL RELATIONS AMONG THE ROTATORY POWERS OF THE COMPOUND SUGARS.*

By C. S. HUDSON.

THE general group of polysaccharides includes many pure crystalline substances of definite chemical individuality, such as the di-, tri-, and tetrasaccharides, together with a series of amorphous products, such as starch, glycogen, inulin, cellulose, pentosans, mannans, galactans, &c. To distinguish the pure crystalline polysaccharides from their less definitely characterised relatives it is suggested that they be classed under the group name of *compound sugars*, a designation which separates them very well also from the simple sugars, or monosaccharides, into which they may be decomposed by hydrolysis. In the present article it is sought to extend to several of the com-

galactose. Other sugars which are now regarded as derivatives of sucrose are gentianose (= glucose < glucose < fructose) and stachyose (= galactose < galactose < glucose < fructose) (Bourquelot and Bridel, *Comptes Rendus*, 1911, clii., 1660). It will be convenient to designate sucrose and its three derived compound sugars as members of the sucrose group. The evidence that gentianose and stachyose belong in the group is not direct and conclusive as in the case of raffinose, though it appears convincing, as will be seen. The action of invertase upon either sucrose or raffinose causes specific hydrolysis of the union between glucose and fructose, which may be designated the *sucrose union*. Invertase may be regarded therefore as a specific hydrolyst of the "sucrose union," and the action of this enzyme upon a compound sugar may be taken as evidence that the sugar contains the "sucrose union," and is a derivative of sucrose. Bourquelot and Hérissé (Journ. Pharm. Chim., 1901, [6], xliii., 305) have shown that invertase splits gentianose into fructose and gentiobiose (= glucose < glucose <), and C. Tanret (Bull. Soc. Chim., 1902, xxvii., 955; see also Vintilescu, Journ. Pharm. Chim., 1909, xxx., 167) has shown that it splits stachyose into fructose and manninotriose (= galactose < galactose < glucose <); hence these sugars are considered to be derivatives of sucrose. Recently, Bourquelot and Bridel (*Comptes Rendus*, 1910, cli., 970) have isolated a new crystalline compound sugar, verbascode, which is hydrolysed by invertase to fructose, and another sugar, not yet isolated; probably verbascode belongs to the sucrose group.

Rotatory Relationships in the Sucrose Group.—The fact that sucrose is not a reducing sugar indicates that the lactonyl hydroxyl groups of its two constituents are bound in glucosidic union, and the further fact that only one molecule of water per molecule of sucrose becomes combined during hydrolysis shows that the groups in question are joined with each other, because if the union were otherwise two molecules of water per molecule of sugar would be used up. The same conclusion may be drawn from the fact that sucrose yields an octacetate, and contains therefore eight hydroxyl groups per molecule. The structure of sucrose is accordingly generally considered to be as shown in the accompanying formula. In this



ound sugars the numerical relationships that have been found to hold among the rotatory powers of the α and β forms of the monosaccharides and their glucosidic derivatives (*Journ. Am. Chem. Soc.*, 1909, xxxi., 66).

Sugars of the Sucrose Group.

(NOTE.—The symbol < denotes the carbonyl or lactonyl group; see *Journ. Am. Chem. Soc.*, 1909, xxxi., 661. The term lactonyl, which has been suggested by S. F. Acree (*Science*, 1915, xlii., 101) to indicate an aldehyde or ketone group that has formed a lactone-like ring, as in the sugars, seems very appropriate).

Known Members of the Group.—The trisaccharide raffinose may be split by complete hydrolysis into its three component simple sugars, galactose, glucose, and fructose; by partial hydrolysis, best through the agency of enzyme action, it may be split either into fructose and melibiose (= galactose < glucose <) by the use of invertase or weak acids, or into galactose and sucrose (= glucose < fructose) by the aid of emulsin. Raffinose may accordingly be regarded as galactose < glucose < fructose, a derivative of sucrose, a combination between that sugar and

formula it is assumed that the lactonyl ring is upon the γ carbon in both hexoses, which appears likely, but the following argument would not be affected if these rings should prove to be in other positions.

(NOTE.—What really is assumed, as will be understood from the continuation, is that the glucose lactonyl ring in sucrose is upon the same carbon atom as in the case of the α and β forms of glucose).

Let G represent the rotation due to the glucose chain, not including, however, the asymmetric lactonyl carbon of rotation B', and let F be the rotation of the fructose residue. Summing these values the molecular rotation of sucrose may be written $[M]_s = G + B' + F$. According to this plan the molecular rotations of the members of the sucrose group may be formulated as follows, when (Mb), (Gb), and (Mn) indicate the rotations of the melibiose, gentiobiose, and manninotriose chains respectively (see Table A). Subtracting the molecular rotation of sucrose from that of raffinose, $[M]_{Rr}$ gives—

$$[M]_{Rr} - [M]_s = (Mb) - G \quad \dots (5).$$

The specific rotation of sucrose is +66.5, and its molecular rotation $(66.5)(342) = +22700 = [M]_s$. In the article first cited it was shown that G may be obtained as half the sum of the molecular rotations of the α and β

* From the *Journal of the American Chemical Society*, xxxviii., No. 8.

TABLE A.

Parent sugar.	Hydrolytic products with invertase.	Molecular rotation of the parent sugar.
Sucrose (mol. wt. 342)	Glucose (180) + Fructose (180)	G + B' + F (1)
Raffinose (504)	Melibiose (342) + Fructose	(Mb) + B' + F (2)
Gentianose (504)	Gentiobiose (342) + Fructose	(Gb) + B' + F (3)
Stachyose (666)	Manninotriose (504) + Fructose	(Mn) + B' + F (4)

forms of glucose, which gives the value +11900 if the specific rotations of the two forms of glucose are taken at 113 (Hudson and Yanovsky, forthcoming publication) and 19 (Hudson and Dale, forthcoming publication). Introducing these values in Equation 5 and transposing gives—

$$(\text{Mb}) = [\text{M}]_R - 10800 \dots (6).$$

To pass now from (Mb) to the rotation of either the α or β form of melibiose it is necessary to add the rotation of the end asymmetric lactonyl carbon atom of melibiose. It has been shown in the former article that the rotation of this carbon is equal to half the difference of the molecular rotations of the α and β forms of glucose, or 8460, hence the molecular rotations of the forms of melibiose are written:—

$$\begin{aligned} \text{Molecular rotation of } \alpha\text{-melibiose} & \dots = (\text{Mb}) + 8460 = [\text{M}]_R - 2340 \\ \text{Molecular rotation of } \beta\text{-melibiose} & \dots = (\text{Mb}) - 8460 = [\text{M}]_R - 19300 \end{aligned}$$

Similar equations with the same numerical terms express the same relation between the molecular rotations of gentiobiose and gentianose, and of manninotriose and stachyose. For the sugars of the sucrose group that are hydrolysed by invertase to yield fructose and an aldose, the molecular rotation of the aldose is less than that of its parent sugar by 2340 for its α form and 19300 for its β modification. The rotatory powers of melibiose, gentiobiose, and manninotriose may be calculated by this relation.

The Rotation of Melibiose—Since the specific rotation of raffinose is +123 its molecular rotation is +62000, and the molecular rotations of the α and β forms of melibiose are calculated from the foregoing relation to have the values +59700 and +42700 respectively, and from these the specific rotations are found to be +175° and +125°. The latter value agrees almost exactly with Loiseau's (*Z. Ver. Zuckerind.*, 1903, lii., 1050) measurement of the initial specific rotation of β -melibiose (124), and recently E. Yanovsky and the writer (forthcoming publication), in repeating the measurement, have obtained the same value as Loiseau. The α form of melibiose has never been prepared in a pure state, and the only experimental value known for its specific rotation is that which Yanovsky and the author have found indirectly through a measurement of the increase in solubility of β -melibiose during its mutarotation. Our value is +179°. The agreement is very good in view of the indirectness of the experimental measurement.

The Rotation of Gentiobiose—The specific rotation of gentianose is +31° (Bourquelot and Nardin, *Comptes Rendus*, 1898, cxxvi., 280), hence its molecular rotation is +15600, and the specific rotations of the α and β forms of gentiobiose may be calculated by the method which has just been followed to be +39 and -11 respectively. Bourquelot and Hérissé (*Journ. Pharm. Chim.*, 1902, [6], xvi., 418) record +9.8 as the final specific rotation of gentiobiose, a value which refers to the equilibrium in solution between the α and β forms of the sugar. By crystallising gentiobiose from methyl alcohol they obtained a crystalline derivative of it containing two molecules of methyl alcohol of crystallisation. This substance had an initial specific rotation in water of about +18, decreasing to +9.8 (both numbers are referred to the solvent-free sugar, mol. wt. 342) on standing. By crystallising gentiobiose from ethyl alcohol solution they prepared the crystalline

sugar itself, which had a specific rotation of -6 six minutes after dissolving, changing likewise to +9.8 on standing. If one extrapolates as well as possible the value -6 back through the first six minutes according to the rate of mutarotation that Bourquelot and Hérissé observed, a value near the calculated -11 is obtained. It would seem that the α form of melibiose which they evidently had in hand in the form of a compound with methyl alcohol of crystallisation contained some of the β modification.

The Rotation of Manninotriose—The specific rotation of stachyose being +148 (Schulze and Planta, *Ber.*, 1890, xxiv., 2705), its molecular rotation is +98600, and hence the specific rotations of the α and β forms of manninotriose are calculated to be +191 and +157 respectively. These rotations do not appear to have ever been measured, but C. Tanret records +167 as the final specific rotation of manninotriose (*Bull. Soc. Chim.*, 1903, [3], xxix., 891). This value lies between the calculated numbers, as should be the case, and is also at approximately the same position between them as in the case of glucose, melibiose, and gentiobiose. The ratio of the concentrations of the β and α forms which are present at equilibrium is for glucose $(113-52)/(52-19) = 1.8$, for melibiose $(175-143)/(143-124) = 1.6$, for gentiobiose $(39-10)/(10+11) = 1.3$, and for manninotriose $(191-167)/(167-157) = 2.4$. If the final rotation of manninotriose were 169 rather than 167 the ratio would be as the same for glucose, and if it were 172 the ratio would be the same as for gentiobiose.

Other possible Members of the Sucrose Group—Since lactose, cellose, and maltose have structures in which the free lactonyl hydroxyl is a part of the glucose group it is conceivable that these disaccharides might be united with fructose through a sucrose union to yield derivatives of sucrose. The expected specific rotations of these compounds can be calculated according to the preceding considerations. For example, since the specific rotation of β -lactose (mol. wt. 342) is +35, its molecular rotation is +12000, and the specific rotation of the hypothetical α -lactose < > α -fructose (mol. wt. 504) is calculated to be $(12000 + 19300)/504 = +62$.

The Acetylated Sugars of the Sucrose Group—Referring back to the structural formula for sucrose, consider the rotation of sucrose octacetate. Its molecular rotation is the sum of a new quantity G', which is the rotation of an acetylated glucose chain, plus B'', which may possibly be different in value from B', plus F', the rotation of an acetylated fructose residue. In the same way that G was obtained from the specific rotations of the α and β forms of glucose G' may be found from those of the corresponding glucose pentacetates (mol. wt. 390), which have the values +102 and +4 respectively in chloroform solution (Hudson and Dale, *Journ. Am. Chem. Soc.*, 1915, xxxvii., 1265). Half of the sum of their molecular rotations is +20700 = G', and half the difference is +19100, the latter being the rotation of the end asymmetric carbon in glucose pentacetate. The specific rotation of sucrose octacetate (mol. wt. 678) in chloroform is +59.6 (Hudson and Johnson, *Journ. Am. Chem. Soc.*, 1915, xxxvii., 2753), and hence its molecular rotation is +40400. The molecular rotation of the glucose pentacetate chain is therefore 19700 less than that of sucrose octacetate or the molecular rotation of α -glucose pentacetate is $(19700 - 19100) = 600$

* Hudson and Johnson, *Journ. Am. Chem. Soc.*, 1915, xxxvii., 2753
† Final specific rotations of the sugars.

less than that of sucrose octacetate, while that of the β -pentacetate is $(19700 + 19100) = 38800$ less. These numerical differences apply also to the molecular rotations of the corresponding acetylated derivatives of the pairs raffinose and melibiose, gentianose and gentiobiose, stachyose and manninotriose. The β octacetates (n.ol. wt. 678) of melibiose and gentiobiose have the specific rotations $+102$ (Hudson and Johnson, *Journ. Am. Chem. Soc.*, 1915, xxxvii., 2752) and -5 (Zempen, *Zeit. Phys. Chem.*, 1913, lxxxv., 402), respectively, in chloroform solution. From these data the specific rotations of the hendecacetates (mol. wt. 966 and formula $C_{28}H_{52}(C_2H_3O)_{11}O_{16}$) of raffinose and gentianose in chloroform are calculated to be $+112$ and $+43$, respectively. Scheibler and Mittelmeier (*Ber.*, 1890, xxii., 1443) have found $+92$ for crystalline raffinose hendecacetate in alcohol, but the value in chloroform is not known. It is probably higher than $+92$, because the specific rotation of sucrose octacetate in chloroform is $+60$ (see preceding) and in alcohol, $+38$ (Herzfeld, *Ber.*, 1880, xiii., 267). Gentianose hendecacetate does not appear to have ever been prepared.

To be continued).

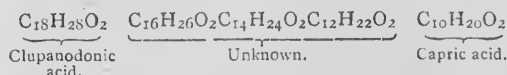
IMPORTANCE OF THE VARRENTRAPP REACTION IN FATS AND SOAPS.*

By WALTER SCHRAUTH.

THE conversion of unsaturated fats and fatty acids into saturated is principally accomplished nowadays by direct hydrogenation in the presence of a catalyser. All previous processes, without exception, have not proved satisfactory in practice. And yet it appears as though one or the other of these processes could be technically carried out with the now available means.

Especially does this apply to the Varrentrapp reaction, by means of which it is easily possible to convert oleic acid by melting with an excess of caustic alkalis into palmitic acid, in accordance with the equation $C_{17}H_{33}COOH + 2KOH = C_{15}H_{31}COOK + CH_3COOK + H_2$. Here occurs therefore with simultaneous hydrogen development, a cleavage of two carbon atoms in the form of acetic acid, whereas the remaining carbon series is oxidised into palmitic acid. This process, which was technically carried out as far back as the seventies of the past century, has subsequently nowhere found adoption, on the one hand by reason of the risks entailed by the development of hydrogen occurring during the reaction; on the other, on account of the high cost it entails. Both reasons no longer hold good, because, in the first place, the industry has accustomed itself to such risks, and on the other hand the cost of the process is much lower when in place of the pure oleic acid cheaper fats are used.

The Varrentrapp reaction is not confined to oleic acid, rather all unsaturated fatty acids are converted, in alkali fusion, into saturated ones of lower carbon-number, and it may be said in such a manner that for each double formation two carbon atoms are split off in the shape of acetic acid. For the clupanodonic acid (with four double bonds) as a result the following formula is obtained:—



Now, clupanodonic acid, which is an important constituent of all train oils, is the cause of the characteristic train oil smell, which, with the progress of the destruction of this acid, must disappear. As a reaction product is

finally obtained a product that displays a certain resemblance to a cocoanut oil soap. Of course, by acidifying the fats, the fatty acids can also be recovered, which on distillation yield a snow-white distillate. The yield amounts usually to about 85 per cent of the fatty acids used (10 to 12 per cent loss through cleaving off of the acetic acids, 3 to 5 per cent through the distillation residue). The melting point of the resultant fatty acids lies between 35 and 40° C.; the iodine number is greatly reduced. The technical possibility of the process is admitted, especially if the process can be carried out with 50 per cent lye in place of the alkali flux. It is certainly necessary that the fatty acids are used because the glycerin in melting would be transformed into exceedingly offensive smelling acrolein.

As apparatus, it is best to use an autoclave of 5000 litres' capacity, into which is placed about 2500 kilos. of train oil fatty acid, and 700 to 800 kilos. of technical caustic soda, which has previously been dissolved in an equal quantity of water. Heat to 200° C., and raise in the course of about six hours to 260° C. The pressure must not exceed ten atmospheres. The mass is then forced as hot fluid into a pan, and here either boiled directly into a marketable soap or worked over for distilled fatty acids.

The addition of an oxidation medium, as prescribed by Riepel in his patent application, can be dispensed with the effect of the alkaline flux being in itself oxidising. The technical effect following the adoption of the Varrentrapp reaction would consist, in the first place, in the saving of cocoanut and palm-nut oil. Hydrogenised train oils are tallow-like, and can only be worked into lathering soaps by the addition of other fats and fatty acids, whereas, according to the process in question, fatty acids are produced, which, in their composition, display a certain resemblance to the vegetable fats. Of course the hydrogen formed during the Varrentrapp reaction can at the same time be used for hydrogenation purposes, and it is thus possible, from the same raw material, the fluid evil-smelling train oil, to find on the one hand a substitute for tallow, on the other one for the vegetable fat.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, February 22, 1917.

Sir J. J. THOMSON, O.M., President, in the Chair.

PAPERS were read as follows:—

"The Fossil Human Skull found at Talgai, Queensland." By S. A. SMITH.

This is a description of the fossil human skull that was shown by Profs. Edgeworth David, F.R.S., and J. T. Wilson, F.R.S., at the meeting in Sydney of the British Association. Although it was found as long ago as 1884, it was not shown to anyone who could appreciate its significance until thirty years afterwards. Prof. David thinks it probable that the human being of whom it once formed a part may have been a contemporary of the extinct *Diprotodon*, *Notelaphas*, *Nototherium*, and *Megalanias*, the fossilised remains of which have been found under similar circumstances and in an identical condition and state of mineralisation in the neighbourhood, though not in the same "billabong."

Before the specimen could be studied, it was necessary to clear away a hard mineral incrustation of carbonate of lime which was coloured with iron salts. It was then found to be the highly fossilised and much fractured skull of a male youth not more—probably some years less—than sixteen years of age.

* Translated from *Deutsche Parfümerie Ztg.*, 1916, in *The American Perfumer*. From the *Chemical Engineer and Manufacturer*, xxiv., No. 5.

The brain-case, the capacity of which was at least 1300 cc., is well within the range of variation of modern aboriginal Australian skulls, to which it presents a very striking similarity in general conformation, as well as in respect of the distinctively Australian characteristics.

But the facial skeleton reveals an important contrast. The exceptionally large teeth—the canines especially—have been responsible for a great development of that portion of the alveolar process which lodges the incisor, canine, and premolar teeth. In respect of this feature the Talgai skull is probably more primitive and ape-like than that of any other known specimen belonging to the human family, excepting only the Piltdown skull, the dental arcade of which that of the Talgai skull, in spite of its immaturity, nearly approaches, not only in actual size, but also in its relative proportions.

The fact that the brain-case had already reached the stage represented in the modern Australian aboriginal, while the face still retained much of the grossness and uncouthness of the ape's, is a further confirmation of the view that, in the evolution of man, the brain first acquired the human status and the refinement of the features came afterwards.

"The Magnetic Storm of August 22, 1916." By C. CHREE, F.R.S.

The paper gives an account of a magnetic storm, accompanied by aurora in Scotland, which occurred on August 22–23, 1916. A comparison is made of the results derived from the magnetic curves at Kew and Eskdalemuir Observatories. The disturbance was much larger at the latter station than at the former. During, however, the most disturbed period, both places afforded a conspicuous example of the type of storm in which the direction of the disturbance vector shows a rapid rotation. During this period the disturbance vector diagram in the horizontal plane was described continuously in a counter-clockwise direction, nearly a complete revolution being effected in the course of one hour.

"Ordinary Convergence of Restricted Fourier Series." By Prof. W. H. YOUNG, F.R.S.

CHEMICAL SOCIETY.

Ordinary Meeting, February 1, 1917.

Dr. ALEXANDER SCOTT, M.A., F.R.S., President,
in the Chair.

THE PRESIDENT referred to the loss which the Society had sustained in the death of Mr. Andrea Angel, who was elected a Fellow on February 15, 1905, and who was killed in the explosion on January 19.

Certificates were read for the first time in favour of Messrs. Beni Madhub Chakravarti, B.A., L.M.S., 2, Beharilal Chakravarti Street, Beadon Square P.O., Calcutta, India; Charles Kilner Crosland, Field Cottage, Bradley, Huddersfield; Gordon Harvey Field, Holmwood, Dolgarrog, Tal-y-Cafn, N. Wales; William Geary, 7, East Park Avenue, Hull; William Mather, B.A., 20, Grange Road, Pendleton, Manchester; William Hyman Pierce, 4, Pembury Road, Lower Clapton, N.E.; James Netherwood Sugden, B.Sc., 12 Burstock Road, Putney, S.W.; Hugh Edmund Watts, B.Sc., Ph.D., Gordon House, Hutton, Essex.

The following papers were read:—

"Chromium Phosphate." By A. F. JOSEPH and W. N. RAE.

"Evidence for the Existence in Malt of an Enzyme Hydrolysing the Furfurouids of Barley." By JULIAN L. BAKER and H. F. E. HULTON.

Ordinary Meeting, February 15, 1917.

Dr. ALEXANDER SCOTT, M.A., F.R.S., President,
in the Chair.

Mr. W. G. Ramsay was formally admitted a Fellow of the Society.

Certificates were read for the first time in favour of Messrs. Kenneth Shallcross Dickinson, The Hoole Pharmacy, Chester; Tom Macindoe McKenzie, Marsh House, Bridge Road, Grays, Essex; Leonard Roger Batten Pearce, B.Sc., 45, Craven Walk, Stamford Hill, N.

The following Certificates have been authorised by the Council for presentation to ballot under By-law I. (3):—Aired Bishop Hitchins, A.M., Ph.D., 2, Dwight Block, Binghampton, N.Y., U.S.A.; Harold Waterland, Agricultural Department, Mano, Sierra Leone.

The PRESIDENT announced that the following changes in the Officers and Council were proposed by the Council:—

As Vice-Presidents to retire—Prof. P. Phillips Bedson and Col. C. T. Heycock.

As Ordinary Members of Council to retire—Dr. G. Barger, Prof. F. G. Donnan, Prof. K. J. P. Orton, and Dr. G. Senter.

As President—Prof. William Jackson Pope.

As Vice-Presidents who have filled the office of President—Prof. H. E. Armstrong, Prof. A. Crum Brown, Sir William Crookes, Sir James Dewar, Prof. Harold B. Dixon, Prof. Percy F. Frankland, Dr. A. G. Vernon Harcourt, Prof. W. Odling, Prof. W. H. Perkin, Prof. J. Emerson Reynolds, Dr. Alexander Scott, Sir Edward Thorpe, and Sir William A. Tilden.

As Treasurer—Dr. M. O. Forster.

As Honorary Secretaries—Dr. Samuel Smiles and Prof. J. C. Philp.

As Foreign Secretary—Lieut.-Col. Arthur W. Crossley.

As Vice-Presidents—Prof. G. G. Henderson, Prof. F. R. Japp, Prof. A. Lapworth, Col. A. Smithells, Prof. R. Threlfall, and Prof. S. Young.

As New Ordinary Members of Council—Prof. H. C. H. Carpenter, Prof. A. Findlay, Prof. A. Harden, and Dr. T. A. Henry.

The PRESIDENT announced that Mr. A. Chaston Chapman would deliver his lecture, entitled "Some Main Lines of Advance in the Domain of Modern Analytical Chemistry," on March 15, and that the lecture entitled "The Principles of Diffusion—their Analogies and Applications" would be given by Dr. Horace T. Brown, F.R.S., on May 17.

Prof. A. Liversidge, Dr. C. A. Keane, and Mr. E. W. Voelcker were elected to Audit the Society's accounts.

Messrs. A. J. Ewins and A. Stevenson were elected Scrutators, and a ballot for the election of Fellows was held. The following were subsequently declared elected as Fellows:—Charles William Brown Arnold, B.Sc.; Samuel Comber Atkinson, B.Sc.; Kumār Nāth Bāgchi, B.Sc., M.B.; His Highness Raj Rana Sr Bhawani Singh Bahadur; Ernest Graham Banbridge, B.Sc.; Frank Bayley, M.Sc.; Sir Hugh Bell, Bart., J.P., D.C.L., LL.D.; Robert de la Poer Berestord, M.D., L.R.C.P.; William Reading Bufton; Percival Joseph Channon; Norman Mederson Comber, B.Sc.; Charles Edwin Corfield; Harold James Cress; Sir William Coats Cross, Bart.; Francis William Buckland Cunningham, B.Sc.; Biman Bihari Dey, D.Sc.; Charles William Dick, B.Sc.; John Dines; John Ernest Dunstan; Reginald George Early; John Fitzpatrick Ferns, M.Sc.; Gilbert Arthur Freak, R.Sc.; Herbert Henry Froyssell; William Douglas Graddon, B.Sc.; Roland Hall; Arthur Austin Hoskings; John Carroll Johnson; John Sydney Kael, B.Sc.; Lionel Frederick Knapp, B.Sc.; Jacob Krizewsky, B.Sc.; Alfred Godfrey Gordon Leonard, B.Sc., Ph.D.; Trevor Owen Morgan, B.Sc.; Ernest William Moss; Herbert Eustace

Nickels; Alfred Nuttall; Walter Parker; Hubert Sutton Patterson; William Payman, M.Sc.; Frank Henry Pugh, B.A.; Gunendranath Raye; George Christie Redpath; Arthur Stanley Reed; Henry Charles Stewart-Carlile; Samuel Sugden; Felix John Tromp, B.A.; John Nicholson Fowler; Allen Whitehead.

The following papers were read:—

"Relation between Chemical Constitution and Physiological Action in certain Substituted Amino-alkyl Esters." (Part II.). By F. L. PYMAN.

"Dehydration of some Hydrated Dye-stuffs." By J. C. PHILIP and A. BRAMLEY.

Annual General Meeting.

The Annual General Meeting will be held on Thursday, March 29, 1917, at 4 p.m., when the retiring President will deliver his Address, entitled "The Atomic Theory."

PHYSICAL SOCIETY.

Annual General Meeting, February 9, 1917.

Prof. C. V. BOYS, F.R.S., President, in the Chair.

THE report of the Council was read by Dr. W. ECCLES.

The report of the Treasurer was read by Mr. W. DUDELL.

Both reports were put to the meeting and unanimously adopted.

Mr. T. H. BLAKESLEY asked why the agenda of the meetings were not published in various papers, such, for example, as the *Journal of the Society of Arts*? This was a useful practice, and was customary at one time.

Dr. WILLOWS explained that at present there was very often a difficulty in obtaining papers until too late for circulation of the agenda to the Press.

Dr. ECCLES pointed out that the printers were short-handed, and that this interfered with the prompt circulation of Press notices.

Votes of thanks to the Auditors, the Officers and Council, and the Governing Body of the Imperial College were carried unanimously, the respective proposers and seconders being Mr. C. C. PATERSON and Dr. G. W. O. HOWE; Mr. T. H. BLAKESLEY and Prof. COLEMAN; Mr. F. E. SMITH and Mr. D. OWEN.

The following is the list of officers elected for the ensuing year:—

President—Prof. C. Vernon Boys, F.R.S.

Vice-Presidents (who have filled the office of President)—Prof. G. C. Foster, F.R.S.; Prof. R. B. Clifton, M.A., F.R.S.; Prof. A. W. Reinold, C.B., M.A., F.R.S.; Sir W. de W. Abney, R.E., K.C.B., D.C.L., F.R.S.; Prin. Sir Oliver J. Lodge, D.Sc., F.R.S.; R. T. Glazebrook, D.Sc., F.R.S.; Prof. J. Perry, D.Sc., F.R.S.; C. Chree, Sc.D., F.R.S.; Prof. H. L. Callendar, M.A., F.R.S.; Prof. A. Schuster, Ph.D., F.R.S.; Sir J. J. Thomson, O.M., D.Sc., F.R.S.

Vice-Presidents—W. R. Cooper, M.A., B.Sc.; Sir Napier Shaw, F.R.S.; S. W. J. Smith, M.A., D.Sc., F.R.S.; W. E. Sumner, D.Sc.

Secretaries—W. Eccles, D.Sc., Finsbury Technical College, Leonard Street, E.C.; R. S. Willows, M.A., D.Sc., the Sir John Cass Technical Institute, Jewry Street, Aldgate, E.C.

Foreign Secretary—R. T. Glazebrook, D.Sc., F.R.S.

Treasurer—W. Duddell, F.R.S., 56, Victoria Street, S.W.

Librarian—S. W. J. Smith, M.A., D.Sc., F.R.S., Imperial College of Science and Technology.

Other Members of Council—H. S. Allen, M.A., D.Sc.; Prof. E. H. Barton, D.Sc., F.R.S.; Prof. G. W. O. Howe, D.Sc.; Prof. J. W. Nicholson, M.A., D.Sc.;

C. C. Paterson; C. E. S. Phillips, F.R.S.E.; Prof. O. W. Richardson, M.A., D.Sc., F.R.S.; S. Russ, M.A., D.Sc.; T. Smith, B.A.; F. J. W. Whipple, M.A.

A paper, entitled, "Note on the Calculation of the Coefficient of Diffusion of a Salt at a Definite Concentration," was read by Dr. A. GRIFFITHS.

In the calculation of the coefficient of diffusion, by B. W. Clack, a simple relation is assumed between the density of a solution of a salt and the concentration. This simple relation is only approximately correct, and compromises are made which require justification.

This note—

1. Suggests a method of calculating the coefficient of diffusion which, to a high degree of theoretical accuracy, gives values for the coefficient which are independent of a precise relationship between density and concentration; and

2. Justifies the method of calculation adopted by B. W. Clack.

DISCUSSION.

Mr. B. W. CLACK—The coefficient of diffusion is not a constant, but varies with the concentration to a considerable extent. In most experimental work the coefficient varies at different positions in the apparatus, and any work which helps towards the proper interpretation of results is of value.

A paper entitled, "A Special Test on the Gravitation Temperature Effect," by Dr. P. E. SHAW and Mr. C. HAYES, was read, in the absence of the authors, by the ASSISTANT SECRETARY.

In the *Phil. Trans. of the Royal Society*, vol. ccxvi., p. 349, there is a paper by one of the authors dealing with the possible existence of a temperature coefficient of the constant of gravitation. It was suggested in the discussion that the effect might be due to an inward displacement of the large lead spheres, at the higher temperatures, due to convection currents.

In the present paper experiments are described in which this point is tested by micrometric measurements of the positions of the supporting wires. It is shown that, at the higher temperatures, there is a small outward displacement of the spheres, probably due to the expansion of the crosshead from which they are suspended. A slightly higher value has therefore to be given to the temperature coefficient of gravitation.

DISCUSSION.

Mr. F. E. SMITH suggested that since it appeared to be necessary to measure the deflection of the large spheres in order to arrive at the correct result, this could be more advantageously done with an arrangement of microscopes than with the micrometers employed.

Prof. C. V. BOYS thought the subject was one of vital importance. He was not yet convinced that the results obtained by Dr. Shaw were necessarily true; but the apparatus was in many ways so beautifully designed that it was difficult to see what could give rise to the discrepancy. It seemed to him that Dr. Shaw's method of measuring the constant at two different temperatures was not the best way of measuring the difference between these values, which was thus subject to the inaccuracy of the complete determination. It seemed a better plan to have two sets of balls, one in the A position and one in the B position, and to measure any change in the deflection produced when one pair were hot and the other cold, and *vice versa*. This would be a null method, and would measure only the temperature coefficient if such existed. He had mentioned this to Dr. Shaw, who had brought forward some difficulty in connection with it which he could not at the moment remember.

Mr. C. C. PATERSON asked if it was not possible for convection currents to be set up inside the vacuum tube and to affect the small spheres.

The substance of the discussion has been communicated

to the authors. Their reply will appear in the *Proceedings*.

Guthrie Lecture.

The third Guthrie Lecture will be delivered by Prof. P. Langevin, at the Imperial College of Science, on Friday, March 23. The title of the lecture, which will be given in English, is "Molecular Orientation."

INSTITUTE OF CHEMISTRY.

Annual General Meeting, March 1, 1917.

Sir JAMES J. DOBBIE, President, in the Chair

IN the course of his Address, the PRESIDENT referred to the services of professional chemists in connection with the war. The high rank which many of the members and students had attained and the distinctions they had won gave the Institute every reason to be proud of the part they had taken in the conflict. The Institute had acted as a chemical clearing-house, assisting public departments and firms engaged on Government work to obtain the chemical service they required. Apart from that, the researches on glass initiated by the Institute, particularly the work of Prof. Herbert Jackson, had proved of great value, and had been specially recognised by the President of the Board of Trade. Progress had also been made with raising the fund for the new premises of the Institute, for which a further sum of £2250 was yet required.

In mentioning the losses sustained by British chemistry during the year, the President referred especially to Sir William Ramsay and his work on rare gases, and Mr. David Howard, Past-President, one of the leaders of British chemical industry.

After indicating a number of new industrial developments which called for the help of practical chemists, the President advocated the extension of the training of chemists, particularly in higher physics and physical chemistry, and therefore the adoption of a four instead of a three years' course. He emphasised the importance of mechanics to chemists who intended to practise in industry, and recommended a training as wide as possible for chemists generally. Dealing with the recent discussions on general education and the reform of the school curriculum, he criticised what was termed "generalised science," by which he supposed was meant a composite course, including a little physics, a little chemistry, a little biology, and a little of everything else, and suggested that school science should be as simple as possible and that the first place should be given to mechanics experimentally treated, as being essential to the study of all other experimental science.

The Officers and Members of Council for the ensuing year were duly elected.

SOCIETY OF CHEMICAL INDUSTRY.
(LONDON SECTION).

Ordinary Meeting, February 5, 1917.

Mr. ARTHUR R. LING in the Chair.

Dr. E. J. RUSSELL, Director of the Rothamstead Experimental Station, read a paper on "*Artificial Fertilisers: their Present Use and Future Prospects*." This paper was in the nature of a lecture giving a *résumé* of the uses of various fertilisers. The author stated that "Artificial Fertilisers" are simple salts, which are added to the soil to help in the nutrition of plants; they are called "artificial" because they have usually undergone some manufacturing process. There are three classes: Nitrogen compounds, phosphates, and potassium compounds; it is useful, also,

to add a fourth: Organic matter: almost anything containing these constituents will serve, the only conditions being that the substance shall not be toxic to the plant, and that it shall be capable of going into solution in the soil-water directly or as the result of decomposition in the soil, so that it can enter the plant roots. In practice, however, a third condition is essential, the price must be sufficiently low, and this rules out so many substances that the actual list of artificial fertilisers is short.

Dealing with superphosphate, the author stated that the industry was founded in this country, but that we had not kept our lead. Before the war, Germany, France, and Italy had all passed us, and Belgium was beginning to catch us up. Superphosphate was most useful when applied to root growth such as swedes, turnips, mangolds, and potatoes. The special effect of encouraging root production and of hastening maturity was very valuable on heavy soils everywhere, but especially in wet districts. It had been shown that superphosphate greatly increased the yield of maize in South Africa, and there were indications in India where its use was just commencing that it was needed for some crops. In Louisiana, the use of superphosphate had sometimes diminished the yield of cotton on poor soil; and this manure did not seem to be wanted for the cane sugar crop.

Of other phosphate manures, basic slag was very beneficial for grass land, and experiments had shown remarkable gains, especially on heavy land, the best known results being those obtained at Cockle Park. Of nitrogenous manures, nitrate of soda owed its popularity as a fertiliser to the circumstance that it was ready for use by the crop and had to undergo no further change. It was, therefore, the quickest in action of all nitrogenous fertilisers. In this country it had been found, as a result of long-continued experiments at Rothamstead, that the superiority of nitrate of soda amounted to about 6 per cent for barleys and hay crops, and was greater for wheat and mangolds than sulphate of ammonia. One distinct advantage of nitrate of soda was that it tended to charge the soil with sodium carbonate, and in the case of a clay soil it rendered it very sticky. This did no harm on light soils or loams. As regards calcium nitrate, further experience was needed before any definite conclusion could be arrived at. With regard to potassium nitrate, this substance was dearer than a mixture of nitrate of soda and sulphate of potash, and therefore was not used in this country. Ammonium nitrate was a most concentrated nitrogenous fertiliser, containing not less than 35 per cent of nitrogen, but unfortunately it was highly soluble and deliquescent, and seriously damaged the young leaves wherever it touched them. Sulphate of ammonia was largely used in this country for potatoes, and also to an increasing extent as a spring dressing for corn. It had two important properties which gave it a definite advantage over nitrate of soda in special circumstances. 1. It did not easily wash out from the soil as it was readily absorbed, and in this state resisted even tropical rainfall. 2. It could still change to nitrate, however, to be taken up by plants. Calcium cyanamide or nitrolin was considered, and it was pointed out that under the influence of lime, alkalis, and acids, it polymerised to dicyanodiamide, which was toxic to plants. Organic nitrogenous fertilisers were then considered. With regard to potassium salts the author pointed out that by far the largest deposits occurred at Stassfurt, and that no other sufficient source was yet in sight.

The lecture concluded with a consideration of the relation of crop yields to the amount of nitrogen supplied, the total amounts of artificial fertilisers used in the different agricultural countries of the world, and a detailed comparison showing amounts of fertilisers used in the chief consuming countries. From these it appeared that we had considerable leeway to make up in this country before we reached the consumption of Germany, and that Germany was far behind Belgium, but we were not so bad as we had sometime supposed. The position of Great

Britain arose not so much from ignorance or prejudice on the part of the farmer as from the circumstance that the fiscal and economic conditions in this country has tended to favour the production of grass rather than of corn and roots, while in Germany and Belgium the conditions had favoured the production of corn and roots rather than of grass. Now grass land only requires a fraction of the manure given to corn and roots, and therefore our system of husbandry called for less fertilisers than that of Belgium or Germany. Our system also produced less food: in peace time that was not supposed to matter, but in war time its weakness was exposed. If a change in our system came, and if it led to less grass and more corn, we should automatically consume larger quantities of artificial manures.

But it was in our Empire that we might look for the greatest increase in consumption. As the experiments show, phosphates and nitrogenous fertilisers brought about large increases in crop production, and it was reasonable to anticipate great expansion in the demand if the supply were forthcoming. This was an alter-the-war problem, but chemists would have no difficulty in seeing its close connection with the present problems of the supply of explosives.

A discussion followed.

"Basic Slag as Affecting Agricultural Development."

By Prof. GILCHRIST, M.Sc., and Prof. LOUIS, M.A.

The authors point out that whilst the wastage of nitrogen may be made good by the growth of leguminous plants, and to a certain extent without the direct addition of nitrogen to the soil, the phosphates removed by the crops must be returned by direct manuring, and farmyard manure does not return these phosphates in a sufficient manner, because so much is retained by the animal. Bones and bone ash were used to some extent to replace the phosphates early in the nineteenth century, and when Liebig and Lewes, about 1840, found that bones and mineral phosphates could be rendered more effective by treatment with sulphuric acid, so as to make part of the phosphates soluble, an enormous impetus was given to the growth of swedes and turnips. When this superphosphate had been used for a considerable time, it came to be realised that this manure did not give as good results on peaty soils or on soils poor in lime as on those in which a fair amount of lime was present.

Until about 1830 the supply of phosphatic manures was met chiefly by superphosphate, produced mainly from mineral phosphates. The Gilchrist-Thomas or basic Bessemer process of steel making, invented about that time, gave basic slag as a by-product, which was soon found to be possessed of valuable manurial properties. Finely ground mineral phosphates were then coming into use, but the cheaper basic slag checked the development of the former as a manure.

The German manufacturers soon succeeded in pressing on the sale of their slag by introducing the citric solubility test. This is of a pseudo-scientific and empirical character and means that citric soluble phosphates are made the criterion of commercial value instead of the total phosphates present. It need hardly be added that this test favours basic Bessemer steel to the disadvantage of all other classes of phosphates, natural and artificial.

In 1913, over 700,000 tons of superphosphate were used for manurial purposes in this country, as well as probably between 200,000 and 300,000 tons of basic slag, along with a certain amount of bones in various forms. The total amount of basic slag of all kinds now produced may be from 800,000 tons to 900,000 tons, and as this amount will certainly be increased in the near future, it can readily be recognised to what extent manuring by basic slag can be developed. The great bulk of the basic slag now produced is a by-product from basic open-hearth steel. This is low grade slag and contains on the average only about 10 per cent phosphoric acid, whereas high grade basic slag, obtained from the basic Bessemer process, may

contain up to 20 per cent of phosphoric acid. The latter responds freely to the citric solubility test, whereas the former does so only to a limited extent. Probably about 700,000 tons of basic slag from the basic open-hearth process are produced in this country annually, a large portion of which is wasted every year, instead of being employed to fertilise our fields, mainly on account of insistence upon the empirical citric solubility test.

The writers summarise the results of field trials of basic slags of high and low citric solubility, and of finely ground mineral phosphates which contain practically no citric soluble phosphates, at Cockle Park, the Northumberland Agricultural Experiment Station, and at other centres in the North of England, and show from these results that the percentages of citric soluble phosphates, apart from percentages of total phosphates, have practically no relation to the manurial results. They strongly urge that the large amounts of low grade basic slag now thrown away should be fully utilised for manurial purposes. They quote results from the Illinois Experiment Station, and from other sources, which show that there was no particular relation between the citric-acid-soluble phosphates and the availability of these for plants, and they urge that the total phosphoric acid content of basic slags is a far more reliable test of their manurial value.

Results from Cockle Park of trials on arable land over rotations of crops and on pasture land, both over a long series of years, show returns from the judicious application of basic slag of from 6s. to 8s. in increased values of crops and pastures for every shilling spent on this manure.

Assuming that 200,000 tons of basic slag are now used for agricultural purposes in the United Kingdom, this provides a dressing of 5 cwt. an acre of basic slag every fourth year for four million acres. If the total basic slag produced in the country were so used (assumed to be equal to 600,000 tons of high grade basic slag) the total area of land so treated would be increased to about 9,600,000 acres, or about one-fifth of the total area under crops and grass in the United Kingdom, and this would result in an enormous increase in the food production of the country.

Investigations are now being made with the object of ascertaining whether high grade mineral phosphates can be added to the basic slag immediately it leaves the open-hearth furnace. If by doing so the mineral phosphates can be given practically the same character as those of basic slag, a high grade basic slag will be produced, which should reach the farmers' nearest railway stations at considerably less cost per unit of phosphoric acid, owing to the saving made in costs per unit of grinding, bagging, and railway carriage.

A vigorous campaign is now being conducted for the reclamation of waste land. This is desirable, but there are far greater possibilities by increasing the output from the land now under cultivation. With little increase in labour this can be largely obtained by the judicious use of basic slag, now largely thrown aside as a waste product, one of the many reasons for this being insistence upon a test which gives results bearing no real relation to its manurial value.

In the discussion, G. S. ROBERTSON drew attention to his field experiments with basic open-hearth slag.

The Röntgen Society.—At the Council Meeting held on February 5, 1917, in view of the satisfactory financial position of the Society, it was unanimously agreed that the Society should purchase £300 War Loan; the Honorary Treasurer was authorised to take the necessary steps to secure the investment. It was also agreed that the Honorary Treasurer and the Honorary Secretaries should be appointed trustees for the loan. In order that all invested funds should be under the same control, it was further agreed that other investments of the Society should be placed under the joint trusteeship of the above three officials of the Society.

NOTICES OF BOOKS.

General Cargo. By RICHARD E. GODDARD. London: Constable and Co., Ltd. 1916. Pp. viii+199. Price 4s. 6d. net.

THE author of this introduction to salesmanship has had business relations with commercial men of most of the civilised countries of the world, and has made a study of the psychology of the nations, so that he is in a position to offer some valuable hints as to how we may attempt to strengthen the state of our trade after the war is over. He gives brief accounts of his views relating to the manners, customs, and requirements of the inhabitants of the chief countries of the world, and his judgments appear to be shrewd and his comments to the point. He has many instances to give of German methods of doing business, and points out clearly the details in which they compare favourably with our own. Our business men have undoubtedly many lessons to learn, and possibly such a book as this will put them in the way of acquiring most necessary knowledge.

A Text-book of Organic Chemistry for Students of Medicine and Biology. By E. V. MCCOLLUM, Ph.D. New York: The Macmillan Company. 1916. Pp. xiii+426. Price 10s. net.

THE short course of organic chemistry for students of medicine and biology given in this book is well planned, and the author has succeeded in making the subject attractive to the beginner; who is sometimes rather bewildered by the usual type of text-book overburdened with details which he finds it almost impossible to assimilate. The pages devoted to the discussion of elementary conceptions are exceedingly clear and well written, and although necessarily a very large number of facts has to be included every effort is made to show their interdependence and to induce the student to trust to his reasoning power rather than to his memory. Many structural formulæ are given, and in every case the facts are stated upon which the formulæ are based. Much attention is paid to those compounds which are of special interest in biology and medicine, and students of these sciences will find the book a really useful and practical guide in their chemical work.

Laboratory Manual of General Chemistry. By ARTHUR B. LAMB. Cambridge, Mass.: Harvard University Press. 1916. Pp. 160+130 for notes. Price 1.45 dols.

THE author's experience has shown him that the average student who has done some work in elementary chemistry at school is very apt to suffer from over-confidence and boredom when he begins his college course. He has probably acquired a more or less superficial knowledge of most of his first term's work, and the problem of how to make the best use of this knowledge is a very difficult one to solve. The process of extending half knowledge often leads to the flagging of interest, which is to be avoided at all costs. The author's scheme of experimental work, in which many new experiments are described, especially such as are of a semi quantitative nature, seems likely to be useful. Very clear and interesting theoretical discussions are introduced, and full references for "assigned" and "suggested" readings are included. The whole is systematically arranged, and the minute directions for performing the experiments and writing out the reports should very materially reduce the task of the demonstrator. The list of preparations is particularly full and includes many rather unusual substances, and the experimental work upon general principles is very well chosen.

Black Damp in Mines. By G. A. BURRELL, J. W. ROBERTSON, and G. G. OBERFELL. Washington: Government Printing Office. 1916. Pp. 88. Price 10 cents.

IN this bulletin the principal factors which affect the changes in mine air, e.g., the velocity of air in the passages, the gaseous (methane) nature of the seam, the temperature, and wetness of the mine, are discussed in detail, and experiments are described in which the proportions of carbon dioxide, which produce harmful effects, were determined. It was found that when the oxygen percentage falls below 13 serious consequences may ensue. Explosive proportions of methane become non-explosive when the proportion of oxygen falls below 14 per cent. Many experiments were carried out to ascertain how mine air changes as it passes through the workings, and the average composition of black damp (90.8 per cent of nitrogen and 9.2 per cent of carbon dioxide) were determined. The bulletin contains much useful and practical information for colliery managers in this country, although all the analyses refer to coal-mines in the United States.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clxiv., No. 1, January 2, 1917.

Absolute Density of Hydrobromic Acid.—C. K. REIMAN.—Hydrobromic acid was prepared and purified by three different methods. It was synthesised from hydrogen, obtained by the electrolysis of a concentrated solution of KOH, and bromine liberated from KBr by potassium permanganate and sulphuric acid. The gas was dissolved in water and the aqueous solution fractionated. By allowing the middle fraction to react with excess of P_2O_5 a regular current of gas was obtained, which was purified by liquefaction and fractional distillation. The synthesised gas was also purified by condensation with liquid air and fractional distillation *in vacuo*. The gas was also obtained by the action of syrupy H_3PO_4 on KBr, and purified by fractional distillation *in vacuo*. The mean of thirty-one determinations of the density was 3.6442 ± 0.0002 grms. per litre.

MISCELLANEOUS.

Royal Institution.—A General Meeting of the Members was held on the 5th inst., Sir James Crichton-Browne, Treasurer, in the Chair. Mr. Seymore Branfort, Mrs. G. Gascoigne, Mrs. Algernon Mansel, and Mrs. R. Frederick Yorke were elected Members of the Royal Institution.

The Ceramic Society.—A meeting of the Refractory Materials Section will be held on March 13 at the Leeds University, in the Lecture Room of the Department of Coal-gas and Fuel Industries. The proceedings will commence at 9.45 a.m.

A Guide to the Registration of Business Names Act, 1916.—A book bearing this title has been written by Kenneth Brown, Solicitor, and will be published immediately by Sir Isaac Pitman and Sons, Ltd., 1, Amen Corner, E.C. It sets forth plainly the obligations placed by the Act on all classes of businesses. The price is 1s. net.

MEETINGS FOR THE WEEK.

MONDAY, 12th.—Royal Society of Arts, 4.30. (Aldred Lecture).
"Memorials and Monuments," by L. Weaver.

Biochemical Society, 5.30. Annual General Meeting.
(In the Lister Institute, Chelsea Gardens, S.W.)

TUESDAY, 13th.—Royal Institution, 3. "Geological War Problems,"
by Prof. J. W. Gregory.

Ceramic Society, at Leeds University. Various
Papers will be read throughout the day, the pro-
ceedings commencing at 9.45 a.m.

WEDNESDAY, 14th.—Royal Society of Arts, 4.30. "The Supply of
Fertilisers during the War," by Dr. J. A. Voelcker.

THURSDAY, 15th.—Royal Institution, 3. "Sponges—a Study in Evolu-
tionary Biology," by Prof. A. Dendy.

Royal Society of Arts, 4.30. "The Industrial and
Economic Development of the Indian Forest
Products" by R. S. Pearson.

Royal Society, "Initial Wave Resistance of a
Moving Surface Pressure," by T. H. Havelock.
"Experiments with Mercury Jets—(1) Relation be-
tween the Jet-length and the Velocity of Efflux;
(2) Comparison with Jets of other Liquids," by S.
W. J. Smith and H. Moss. "Mode of Approach
to Zero of the Coefficients of a Fourier Series,"
by W. H. Young. "Dissipation of Energy in the
Tides in connection with the Acceleration of the
Moon's Mean Motion," by R. O. Street.

FRIDAY, 16th.—Royal Institution, 5.30. "Scientific Forestry for the
United Kingdom," by Sir John Stirling Maxwell.

SATURDAY, 17th.—Royal Institution, 3. "Imperial Eugenics—Saving
the Future," by C. W. Saleeby.

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Act, advertisements from firms whose business consists
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THE CHEMICAL NEWS

VOL. CXV., No. 2990.

THE TRAINING AND WORK OF THE CHEMICAL ENGINEER.*

By Sir GEORGE REILBY, LL.D., F.R.S

WAR has given an altogether new significance to the position of chemistry in relation to the national life. To some of us the development of chemical industries and the training of men willing and able to take part in this development were ever present problems long before these questions were forced to the front by the necessities of war, but the number of those interested has of late been enormously increased.

While the war has done a very real service in thus pressing these questions on the attention of a wider circle and with an urgency which cannot be ignored, there is undoubtedly a danger that the urgent call for chemists to man the factories, old and new, which are turning out explosives and other chemical munitions of war, and the further call to the front of men required for the conduct of chemical trench warfare, both on its offensive and defensive sides, has resulted in the complete depletion of students at our universities and colleges, from whose ranks fully-trained workers for post-war conditions would naturally have been drawn.

There is also a very real danger that the present war conditions may encourage the development of unbalanced proposals for the training of the future leaders and workers in industry. In view of these actual and possible dangers we ought to feel indebted to the President and officers of the Faraday Society for giving to all who are interested in the solution of these problems this opportunity for an exchange of views on the important questions which are involved.

I have been asked by the President to speak on the Functions and Training of the Chemical Engineer, but before attempting to deal with these subjects it is desirable that we should make the general relation of chemical engineering to industrial chemistry as a whole more clear. The chemical engineer will undoubtedly have to play a very important part in industry after the war, but we must not allow ourselves to forget that he is, after all, only one particular kind of specialist, whose functions only cover one part of the field occupied by chemistry in its industrial applications. As one of the earliest users of the term "chemical engineering," it may be well that I should at the outset state very clearly the meaning I have always attached to the expression.

Chemical engineering has for its function the design and construction of apparatus required for the carrying out of chemical processes on a manufacturing scale.

At this stage I will not enter into the reasons which justify us in regarding chemical engineering as a real and definite branch of engineering—that will be done later; for the present let it be assumed that this position is accepted. We can now state quite clearly what portions of the field occupied by chemistry in its industrial applications are not covered by chemical engineering. The centre of all chemical activity is in the laboratory. The discovery of new and improved processes, the investigation of the causes of failure and inefficiency in the factory, the organisation of analytical control of raw materials and finished products, and the preservation of statistics and

records are all initiated and controlled from the laboratory. In considering the activities of the laboratory, it is evident that these are of two types. For the first of these the qualities required in the chemical staff are, wide scientific knowledge, originality, and resourcefulness; for the second, sound chemical training, method, quickness, and organising power. The remaining portion of the field to be covered in the factory is the process control. In the future it is inevitable that the control of the processes in the factory will tend to pass more and more into the hands of trained chemists, but it must be recognised that no amount of purely scientific training will produce the right type of man for this duty; indeed, it is easy to over-train a man by leaving him too long amidst purely academic surroundings. The laboratory training in chemistry tends to produce a certain narrow individualism which may be a serious disqualification for the work of the factory. It is partly as a corrective to this narrow individualism that I strongly recommend the inclusion of a certain amount of engineering training in the education of the majority of those who propose to take up the work of industrial chemistry. I say "the majority" advisedly, because I hold very strongly that in the later years of the four years' course which ought to be regarded as the absolute minimum required for all serious chemists, the heads of the department in university and college training laboratories ought to be in a position to differentiate the various leading types of students into investigators, routine workers, and men of administrative ability. The heads of the engineering department might on their part pick out from the chemical students passing through their hands those who show mechanical aptitudes in any particular way. The last proposal brings us naturally to the first step in the selection of the future chemical engineer. After the third year of chemical and general scientific training, students who have shown special aptitude in engineering might be given special facilities for gaining engineering experience in the workshop and drawing office. The method of late specialisation will ensure that the future engineer is so well grounded in chemical theory and methods that he will run no risk of losing the chemist's point of view during his subsequent engineering training. This object will be further helped by special laboratory courses in the engineering of chemical processes which will serve to keep his chemical knowledge alive.

The scheme thus outlined for the training of chemists for industry may now be briefly summarised:—

1. A sound and practical training in chemistry and chemical physics extending over three years. During the third year special subjects to be introduced.
2. At the end of the third year at latest the case of each student to be considered by the heads of departments, so that he may be advised in what direction he should specialise.
3. Average students with no special bent to complete their course by general advanced studies during the fourth year.
4. No degree or "hall-mark" to be given in chemistry till the complete four years' curriculum has been taken.
5. Chemical engineers, research chemists, and specialists in other branches to devote one or two years to higher post-graduate study.

We may return now to the functions of the chemical engineer, namely, the design and construction of apparatus required for carrying out chemical processes on a manufacturing scale. To fulfil these functions the chemical engineer must have at his command a great deal of knowledge and experience which is quite outside of the range of the ordinary engineer. Not only must he have at his command a sound knowledge of chemical phenomena and laws, but he must be able to see chemical problems from the chemist's point of view. The conditions of design and construction are largely determined by the properties and condition of the great variety of substances which may be employed in chemical processes.

* An Introductory Address to the General Discussion on "The Training and Work of the Chemical Engineer," held by the Faraday Society, March 6, 1917.

There are very few of the eighty to ninety chemical elements which may not at one time or other be used in manufacturing processes. They may occur as solids, liquids, or gases. The temperatures employed may range from -180°C . to over 2000° , and the pressures may range from an almost perfect vacuum to hundreds of atmospheres. The thermal changes due to the reactions may be of extreme slowness or may be liable to occur with explosive violence. As all reactions are either endothermic or exothermic, the removal of heat from the reacting substances or its addition to them often gives rise to problems of the greatest difficulty in the design of large-scale units. Probably, a greater number of chemical processes have failed on this account than for any other single reason. Many of the gases and liquids handled are highly corrosive and attack all the ordinary materials of construction. Others are either violently or subtly poisonous. Complex liquids have to be separated into their constituents by fractional distillation or condensation, solids to be separated from liquids and gases, and liquids from gases. The materials of construction used for apparatus may have to withstand mechanical stresses of a high order as well as great extremes of temperature.

In electro-chemical processes new conditions are superadded to those referred to above.

For the general lay-out of the factory, for boiler and power houses, and for the transport and mechanical handling of materials, the general engineer may quite well be the better man, but this in no way weakens the case for the specialist.

Having thus briefly run over a few of the outstanding points in the special knowledge required by the chemical engineer, let us turn our attention for a few minutes to the further need referred to at the outset, namely, that the chemical engineer ought to know from within the chemist's point of view as well as the engineer's.

The engineer and the chemist both deal with matter and energy, but they approach these fundamental realities from opposite sides. The engineer starts with matter in its massive forms and with energy as it affects matter in masses. The chemist starts with the molecule, and he deals with energy changes as they affect molecules and molecular groups. It is the chemist alone who has resolved the complexity of terrestrial matter into some eighty or ninety chemical elements, and it is he alone who has determined the conditions under which these elements combine to form an almost infinite number of compounds. He alone has determined the energy changes involved in the association and dissociation of atoms and molecules, and it is his researches on these energy changes which have supplied a mass of fundamental data which have been used in the development of the doctrine of the conservation of energy.

The chemist's starting point does not preclude the possibility of his thinking of matter and energy from the everyday point of view, but it does tend to colour his thoughts when he has to deal with specific problems. When these problems have to do with industrial matters there is a distinct danger that his intellectual sympathies may bias his judgment on practical questions. In a certain sense the training of chemists has been intellectual rather than practical, all knowledge in this sphere being regarded as an end in itself rather than as a means to some more practical and everyday end. To the engineer is given the task of moulding and controlling matter and energy in their various forms for the use and convenience of man. The final verdict which determines his success or failure is given by the users of his appliances or operations, by those for whose safety, comfort, or convenience he is called upon to cater. From the outset of his career, therefore, the engineer has to face the most crucial tests of his work, for in everyday life no measure of intellectual success will lead to the condonation of practical failure. The point of view of the engineer is, therefore, not so far removed from that of the ordinary intelligent person that the latter cannot grasp in a general way his aims and

objects; but the thoughts and aims of the chemist are for the most part quite inscrutable to the vast majority of his fellow-men.

The successful engineer does not, as a rule, take the standpoint of the chemist seriously, and, so far as my experience goes, it is only very rarely that the engineer gets so far into the inner circle of chemistry that he can himself look at chemical problems from the chemist's point of view. On the other hand, it is not so unusual for a trained chemist who has some natural aptitude in mechanical matters to acquire the engineer's point of view. It is this fact which justifies the inclusion of as much engineering as possible in the training of chemists for industry. In this way those students who have the natural aptitude may have the opportunity given them of developing that aptitude. From among the students who in this way have acquired both points of view will be recruited the true chemical engineers, men who can translate processes from the laboratory apparatus into that of the factory. No hard-and-fast rule can be laid down, but if the arguments advanced above are sound, it follows that as the chemist's views of matter and energy are much further removed from everyday notions and conceptions than are those of the engineer, it is wiser first to imbue the mind of the student thoroughly with the more difficult, because less ordinary, point of view.

OUR ANALYTICAL CHEMISTRY AND ITS FUTURE.*

By W. F. HILLEBRAND, Ph.D.,
Chief Chemist of the Bureau of Standards, Washington, U.S.A.

(Continued from p. 112).

WHILE I believe now quite as strongly as I did twelve years ago, that our educational institutions are not doing their full duty by their students in respect to the analytical branch of chemistry, I see no way by which the situation is to be relieved much under the prevailing educational system. Classes are too large and competent instructors too few for that individual oversight which is so essential to the attainment of the best results, and too little time can be devoted to analysis by students because of the multifarious demands made upon them in other directions. The conditions are far different from what they were, for instance, in Bunsen's laboratory, when students averaged two or three lectures a day and ambitious ones put in nearly all the rest of six days a week in the laboratory free from the harassing incubus of impending term examinations. This comparison is not made in a spirit of complaint, but merely to contrast ideal conditions, that have probably passed away even in Germany, with those which we have to face.

If the defects noted are to be corrected in a measure, I see no way by which to accomplish this except by increasing the number of teachers and by extending the period of academic instruction, especially for those who contemplate following the most intricate art of analysis professionally and not merely as a prelude to something else which may bring greater financial returns. The adoption of this course, so often suggested, seems rather remote, yet it should certainly be adopted if we are ever to have a really competent body of instructors. As instructors they would enter upon their teaching career with better preparation and wider experience, but this alone is not enough. Time should be accorded them, while teaching, to gain further experience in all manner of analytical procedures and to keep abreast of the advances made in the art of analysis. The benefits that would follow such changes would soon be manifest, but I doubt much if the exacting requirements of a great deal of our

* The Chandler Lecture, 1916, delivered before the Columbia University, U.S.A.

analytical practice would be fully met by them, so additional aids would still be welcome.

One of these aids we now have to a limited extent. I refer to the use of standard samples, such as are issued by the Bureau of Standards, following the practice for some time in vogue in the iron and steel industry particularly. The larger number of these samples, as most of you know, have been analysed by eight to a dozen chemists who are expert in a given field of analysis and the averaged results are supposed to represent as closely as may be the actual composition of the material as a whole or as to certain of its constituents. If a chemist is able to analyse one of these samples correctly it may be presumed that his technique is good and that the results he obtains on the same type of material of unknown composition are to be trusted. If not, then either his technique or his methods are at fault.

In addition to these analysed samples, the Bureau of Standards has issued several single chemical substances (thus far only compounds of carbon) of the highest attainable purity, which serve as standards for volumetric or polarimetric analysis, or for calorimetry.

The value of such aids as these to the analyst has been very great, and not only in the ways indicated. In connection with their analysis, prior to issuing them, many interesting observations have been made upon the relative values of various methods in common use. Our experience at the Bureau of Standards, extending now over a number of years, have shown that these methods are not all of equal trustworthiness, and that one or another of them is affected by hitherto unsuspected errors, either inherent in the method as practised or introduced by the presence of an unlooked for element. The errors so detected may be very small and for some purposes negligible, but their existence is a disturbing feature and one which is sometimes of moment. A few illustrations will suffice to make this point clear.

1. There are several methods that are in daily use for the determination of phosphorus in steel. Most of them depend on the precipitation of the phosphorus as ammonium-phosphomolybdate and many are the articles that have been written bearing on the proper conditions for forming and washing the precipitate. The wash liquid used in the alkalimetric method, which is probably the most widely employed of any of the methods, is a 1 per cent solution of potassium nitrate. Work done at the Bureau of Standards recently has shown that the solubility of the phosphorus-bearing precipitate in this wash solution, even in the absence of vanadium, is considerably more than has been suspected. In fact, on a high-phosphorus product, if an attempt is made to wash until the washings are neutral, the result may be several hundredths of 1 per cent low. This appears to be true whether the phosphomolybdate is precipitated in presence or absence of iron.

2. The so-called evolution method for determining sulphur in iron and steel is one very much in vogue in industrial laboratories because of the short time required for the determination. In it the sulphur is driven out, mainly in the form of hydrogen sulphide, by boiling the alloy with hydrochloric acid, and collected in a solution of a cadmium salt with a view to determining the sulphur by titration with iodine. The method suffers, however, from defects, some of which are understood but others not, as is evidenced by the very discordant results that are reported by different analysts upon the same sample. So far as can be determined the most discordant results are sometimes obtained by analysts who seem to follow precisely the same procedure. Evidently there is room here for some critical research.

3. Manganese is determined in irons and steels by several methods, of which the bismuthate method affords perhaps the most concordant results in different hands when carried out according to certain closely prescribed details of manipulation and standardisation of volumetric solutions. There is still doubt, however, as to just what

the conditions should be for obtaining a correct end-point in the titration.

4. The methods in use for the determination of tungsten in ferro-tungsten failed completely in a particular instance that was brought to my attention by the chemist of a large steel plant. Works and commercial analysts differed by several per cent in their reported results. A partial explanation for the disagreement was afforded by finding columbium to be present in the alloy, an element hitherto unnoticed and unsuspected in such material. Attempts to devise a convenient and accurate method to meet the conditions have not been very successful, so far as I am aware. Here, again, is room for an interesting study.

5. In the analysis of a brass, one of the Bureau of Standards' series of analysed samples, somewhat discordant results for lead were reported by different analysts. It was found that those results which had been obtained by depositing the lead electrolytically on the anode as peroxide involved a slight error by reason of co-precipitation of small amounts of silica and stannic oxide, these having been present presumably in the colloidal form in the solution as residuals from the separations that had preceded.

These examples show what a wide field there is for studies of a very refined character upon many of the methods that are in wide use before it can be said that we really know them.

Useful as standard samples are, those which are employed as actual checks upon analysis do not fully meet our needs. They do not tell the analyst wherein the defect of his method may lie, if defect there be. How then may we hope further to benefit the increasing body of industrial and commercial analysts, and instructors as well, who have no time for trying out methods of direct determination or of separation, the latter involving often more difficulties than the former?

Before attempting to answer this question I must take up the subject of standard methods of analysis. By a standard method is meant, in a restricted sense, one which has been put forth by a body of recognised standing, usually a committee acting under the auspices of some technical organisation, for use in determining the value of a particular kind or type of material. This country has taken a decided lead in the direction indicated. The following quoted paragraphs are repeated from a paper yet to be published in full that I presented to the Second Pan-American Congress nearly a year ago.

"Most by far of the so-called standard methods are so by virtue solely of their having been put forth as such in a commendatory way by some organisation without imposing any obligation on any one to follow them. This condition takes away much of their standing in comparison with those methods of which the use is binding upon any body of chemists. There are, again, those methods which have been proposed as standards by individuals and are generally without organised backing. It is thus evident that discrimination must be exercised in deciding which of the very many methods put forth as standard have any claim to be considered such.

"The main arguments against standardising methods have been:—(1) That the individuality of the analyst should not be suppressed; (2) that to make methods standard would tend to prevent their improvement and to discourage search for better methods; and (3) that a given method may be applicable to a given material only within a narrow range of its possible compositions, as illustrated by pig iron and steel.

"The answer to the first of these objections is that experience has shown abundantly that for commercial purposes good agreement among analysts is seldom to be hoped for unless each worker uses the same method in which every step and condition of the procedure has been minutely prescribed. It is for commercial purposes that standard methods are most needed, and they need not always be the most exact methods if the latter require the

expenditure of time so great or the employment of apparatus so expensive as to defeat the end in view. For many umpire analyses and for those upon whose results no commercial transactions are dependent, the analyst has ordinarily full liberty of choice.

"The first part of the second objection rests upon a misapprehension. In the minds of those who were pioneers in the movement for standardisation it was probably never contemplated that methods once adopted should endure beyond the life of their usefulness. Either the committees responsible for them would revise them as occasion demanded or new committees would undertake their revision. This is the trend of intention here in the United States and undoubtedly wherever standard methods have obtained a foothold. It is, further, inconceivable that the establishment of standard methods should tend to discourage attempts to improve them or to substitute better ones in their place. If, in the opinion of its users, a method had become unequal to the demands it was expected to meet, considerable credit would accrue to him who should bring it up to the later requirements or secure the adoption of a better. Such incentive would always suffice to prevent stagnation in the stream of analytical progress.

"The third objection must be admitted to be well taken, although it suffices in no way to secure the condemnation of standard methods in general. The difficulty referred to under (3) above has been well covered by Dr. Dudley in collaboration with Mr. F. N. Pease in their paper read before the World's Congress of Chemists at Chicago in 1893 (*Journ. Am. Chem. Soc.*, 1893, xv., 501). Their remedy—a partial one only—calls for employment of a variety of standard samples for a given material, covering adequately its usual range in composition, of each of which samples the composition has been determined accurately. Iron and steel are examples of this kind. If then, by applying his method to the particular standard sample which lies nearest in character and composition (mineral as well as chemical) to the material he is to test, the analyst obtains correct results, he is usually justified in concluding that the results he gets in the ordinary course of work upon similar material are also correct.

"The use of standard samples does away in a measure with the need of standard methods, for any method that will yield the true composition of the standard is a suitable one for a given analyst. Even so, it is usually only when this acceptable method is employed with strict adherence to a certain procedure that it yields a correct result. Thus prescribed and limited by a competent authority it may become a standard method for use in all hands. Nevertheless, a standard method is not always applicable to a complex material throughout the whole range of its possible compositions. In such case modifications of the method must be used suited to the special conditions, or different methods altogether are called for. The determination of the need for such variations or changes is one of the duties of the committees entrusted with the choice or formulation of standard methods. These committees have also to consider, in special cases, the need of a refined method for umpire work, and of another less detailed for work of a more routine character."

The principles which should lie at the basis of a standard method have been stated by me in a paper on "Standard Methods of Sampling and Analysis and Standard Samples" (*Journ. Ind. Eng. Chem.*, 1916, viii., 466), as follows:—

1. That its limits of accuracy and its applicability are clearly defined and understood.

2. That it should yield sufficiently accurate and concordant results in the hands of different analysts.

3. That it should not demand such close adherence to detail or such manipulative skill and judgment, or such time consumption as to affect seriously its usefulness.

4. That it should have been tested upon material of high purity or upon material carefully analysed by independent and reliable methods.

5. That the results obtainable upon a given class of materials should not be too dependent upon the composition (steel, iron).

These principles, however, have been seldom rigidly observed as to the methods hitherto offered. Having been prepared as a rule by different bodies of men of varying calibre and judgment, and sometimes by compilation of existing data rather than by direct rigid experimentation and trial, the methods are of very unequal merit. No argument seems to be needed to support the assertion that the preparation of such methods should be entrusted only to men of much experience and sound judgment, who have ample time to devote to most critical study of them. Unfortunately, this last condition is one that it is seldom possible to meet. The consequence is that too often the results do not measure up to the high standard that should attach to such methods. Nevertheless, an admittedly imperfect method is better than none if its limitations are well understood, for it affords a better basis for fixing the value of many articles of commerce than a variety of methods of uncertain relative and even absolute merit.

There is another requirement, however, without which the best of standard methods will avail little, namely, reagents of uniformly high quality. The need for enforceable specifications for reagents has long been apparent and the American Chemical Society at one time endeavoured to bring about improvement in the quality of reagents. It is unnecessary to go into an exposition of the reasons why comparatively little came of this attempt. Some promise of relief seemed to be afforded, however, by the appearance on the market of "analysed" or "tested" reagents, the bottles bearing statements of the nature and amounts of impurities present, or that certain possible contaminants were absent. But it soon appeared that these statements could not be taken at their face value without risk, and the situation is particularly deplorable just now. The following recent observations are worth recording.

In sodium carbonate purporting to be free from phosphorus and silica both were present in amounts which condemned the reagent utterly for a variety of uses. Sodium hydroxide was found to be very impure, in marked contrast with the statement on the bottle. Sodium sulphide contained not only much thiosulphate or polysulphide but was black with iron sulphide, although said to be free from iron. Lead chromate, alleged to carry 0.0003 per cent of nitric acid, held 7 per cent of lead nitrate.

No condemnation is too severe, even in the present times of stress, for the manufacturer who so mislabels his wares. We certainly need a new law or an extension of the Pure Food and Drugs Act to protect the chemist.

Committee work, then, as hitherto practised does not conduce to the production of results of consistently high standard. My experience makes me feel strongly that the advances to be expected through committees of professional societies are too often slight, and are secured at a cost of time and effort quite incommensurate with the gains. This is especially true because:—(a) It is difficult to hold the necessary frequent conferences of members widely separated, from which it results too often that the approval of a society is given to what is practically one man's work; (b) the members of committees sometimes lack a real conception of what a standard method should be in the light of the criteria by which they should be judged; (c) if competent in this respect, the members are not often able to devote the needed time to actual and painstaking experimental work; (d) different methods are in the hands of different committees, without direct control by some head which has authority and is competent to see and direct that the fundamental principles are observed and followed in each and every case, to the end

that the results shall be uniformly of high grade and consistently reported.

These and other considerations lead to the conclusion that such work should be in the hands of a permanently constituted body of well-salaried men under a director of the very highest ability as an analyst and of excellent tact and judgment. These men should be appointed only with the expectation that they are entering upon their life-work. It should be the intention to retain at all reasonable cost the services of those who prove thoroughly acceptable. Acceptability includes of course not only analytical skill, but also diligence, absolute honesty, and the highest conception of the dignity of this work. The beginnings of such an enterprise would be beset with uncertainties and the output not always of the desired quality, but as the men gained experience and insight into the fundamentals of their general work, improvement would come and in the end there would be gathered in this institution a band of men of unrivalled experience and knowledge, whose recommendations would carry such weight that little hesitation would be manifested by technical societies and legislative and industrial bodies in giving them their formal and practical sanction.

But the field of work for an institution of this kind should not be restricted to the comparative study of different methods that are applicable to the determination of one or more elements in a given class of materials, such as irons and steels, brasses and bearing metals, but should include the preparation, analysis, and issuing of standard samples of many kinds, both commercial articles for direct checking of analysis and pure substances and solutions intended for calorimetric, volumetric, and other uses.

Furthermore, and this is very important, the institution should not act independently of the many industries which it is established to aid, but should tactfully maintain the closest and most sympathetic relations with them all, inviting indeed co-operation of the most intimate nature. Such co-operation would be very valuable oftentimes in exposing difficulties, and thus indicating the directions which research in the central laboratory should take. It should include occasional visits to and from the laboratories of one side and the other for consultation and the actual carrying out of analytical operations, whereby misunderstandings may be sometimes cleared up and the causes of differences ascertained more readily than by any amount of correspondence.

The institution should also be a court of last resort in disputes as to the value of articles of commerce that are subject to chemical test, not only as to the correct chemical composition but also with regard to the causes for the differing results reported by others, and, in general, should be a clearing house of information and a source of inspiration in all that relates to chemical analysis.

(To be continued).

THE COMMERCIAL METERING OF AIR, GAS, AND STEAM.*

By JOHN LAWRENCE HODGSON, B.Sc., Assoc. M.Inst.C.E.

THE paper first discusses the various bases which are suitable for the measurement of compressed air supplied in bulk, and emphasises the desirability of measuring in energy rather than in weight or volume units. The basis of measurement adopted by the Victoria Falls and Transvaal Power Company and by the Rand Mines, Limited, was the quantity of air which would be compressed from mean atmospheric pressure and temperature on the Rand to the pressure of delivery by the expenditure of the

energy represented by one kilowatt-hour in an isothermal compression process of the same overall efficiency as that which obtained between the indicated power in the steam-cylinders and the air delivered in the case of certain specified compressors then in use upon the Rand; it being understood that these compressors should be put in first-class order for the purpose of the test, and run under normal conditions as regards speed and pressure.

Descriptions of the meters and overload devices designed by the author for use in connection with the Victoria Falls and Transvaal Power Company's air supply scheme on the Witwatersrand are then given. Two types of meter were used in connection with this scheme; in that supplied to the Power Company a Venturi tube was used, and in that supplied to the consumers a weighted gate placed in the air-way.

The more interesting parts of these meters are described; including the arrangements whereby the various factors upon which the energy required to compress the air delivered at each point of supply depends are measured and combined so as to give a counter and diagram record of the energy passing; the bell, which is sensitive to a Venturi head of less than $1/10,000$ lb. per square inch and which will measure Venturi heads up to 0.85 lb. per square inch; the pressure diaphragms, by means of which a powerful movement is obtained from a small change in the pressure; and the air-driven centrifugal escapement by means of which the integrating gear is accurately timed.

Two types of overload device are then described; the one cutting off the flow if the maximum discharge contracted for is exceeded; the other throttling the discharge when necessary, to limit it to the maximum contracted for. These overload devices are so arranged that they can readily be set to cut off or to regulate (as the case may be) at various maximum flows within their range. The illustrations given include diagrams of the various parts referred to, and of a typical meter installation on the Rand.

The paper next describes the testing plant which was specially built for calibrating these meters by Messrs. Fraser and Chalmers to the specification and under the supervision of Mr. A. M. Robeson, Mr. A. Smart, and the Author, and which is now re-erected at Ferreira Deep on the Witwatersrand and forms the standard air-testing plant for South Africa.

Details are given of the large displacement meter which forms part of this plant, and which is capable of passing 1200 lbs. weight of air per minute, and of the precision manometer, by means of which differential pressures can be measured over a large range to within $1/1000$ inch head of oil.

The relation between liquid and gaseous discharges through the same nozzle is then discussed, and it is shown, for various typical nozzles and orifices, how the gaseous discharge can, under certain conditions, be calculated if the liquid discharge is known. A table is given which shows how the economy in the power required for testing meters or wind-resistance models diminishes with the density of the fluid used.

The importance of designing the discharge nozzles of "fair shape," if the theoretical discharge-formulas are to be used to obtain the discharge, is emphasised.

The results of the author's experiments on the variation of the discharge coefficient for different types of nozzles and orifices for various values of the ratio of the upstream to the throat pressure are stated.

The experimental discharge coefficient for square-edged orifices placed in a bored pipe line is given, and the necessity for the careful placing of the pressure holes, and for geometrical similarity, is emphasised. A set of curves which show the rapid variation of the pressure of the fluid in the vicinity of the orifice is given. The work on square-edged orifices was carried out by the author in order to obtain an easily reproducible standard of air measurement, but he prefers to use round-edged orifices for commercial

* Abstract of a paper read at the Institution of Civil Engineers, March 6, 1917.

work on account of their smaller liability to be damaged by erosion or careless handling.

The difficulties met with in measuring pulsating flows by means of nozzles and orifices are next discussed, and tables are given which show for three typical wave-forms of various amplitudes, and for two different laws of damping, the nature and the approximate amount of the error likely to occur in the measurement.

Other meters described are:—(1) A meter by means of which pulsating flows of any wave-form and amplitude may be accurately measured. (2) A meter designed by the author for general mining work. This is extremely simple in construction, and is easily handled and installed and maintained. It can be arranged to register in weight, volume, or energy units, as required. It will measure such pulsating flows as are met with in practice with sufficient accuracy, and it corrects automatically for variations in pressure. (3) A steam-metering instrument designed by the author. (4) A gas-meter which has been very successfully used for the metering of large volumes of gas. It will measure down to one-twelfth of full load, and, unlike all other gaseous meters which depend upon a differential pressure measurement, the registration of this meter is independent of the density of the gas passing.

The paper is accompanied by an appendix in which the necessary calculations and theory are given.

SOME NUMERICAL RELATIONS AMONG THE ROTATORY POWERS OF THE COMPOUND SUGARS.*

By C. S. HUDSON.

(Concluded from p. 114).

Sugars of the Trehalose Group.

Trehalose and Isotrehalose.—Since trehalose is not a reducing sugar, combines with only one molecule of water per molecule of sugar during hydrolysis, and also forms an octacetate, its structure may be considered to be *glucose* <> *glucose*, the lactonyl hydroxyls being united with the elimination of water. The three possible combinations which fit this structure, assuming γ lactonyl rings, are α -*glucose* <> α -*glucose*, the α,β form or the β,β form. If G represents the rotation of the glucose chain, as before, and A' that of the asymmetric lactonyl carbon (+A' for the α -glucoside form and -A' for the β) the molecular rotations of the three combinations may be formulated:—

α,α -Trehalose ..	$G + A' + A' + G = 2G + 2A'$
α,β Trehalose ..	$G + A' - A' + G = 2G$
β,β -Trehalose ..	$G - A' - A' + G = 2G - 2A'$

The value of 2G has already been found from the sum of the molecular rotations of the α and β forms of glucose to be +23800, and hence the specific rotation of α,β -trehalose (mol. wt. 342) is calculated to be +70. This value is entirely different from the observed specific rotation of trehalose, +197, hence the natural sugar is not the α,β combination. Neither can it be the β,β form because it should then be less dextrorotatory than +70, since the value of -A' for the known β -glucoses is a quantity of considerable magnitude. On the other hand, the high dextrorotation of trehalose agrees well with what would be expected for α -*glucose* <> α -*glucose*. Assuming this to be the structure of the natural sugar, its molecular rotation ($197 \times 342 = +67400$) is $2G + 2A'$, and since $2G$ is +23800, $2A'$ is +43600, and the molecular rotation of β,β -trehalose ($2G - 2A'$) may be calculated to be -19800, and the specific rotation -58. Under the name

isotrehalose, Fischer and Delbrück (*Ber.*, 1909, xlii., 2776) have recently described a sugar of the trehalose type which they prepared by the saponification of crystalline *isotrehalose octacetate*, a substance which in its turn was made by the condensation of bromo-acetyl glucose. *Isotrehalose* was not obtained in a crystalline state, and the amorphous substance was not free from ash. Under such conditions the specific rotation of the impure material can only be considered as an approximate value of the rotation of the pure sugar. Fischer and Delbrück found -39, a value which strongly suggests that *isotrehalose* is β,β -trehalose. This view is supported by the fact that all other derivatives that have been prepared from bromo-acetyl glucose belong to the β series. It is also supported by the result of the following considerations, which indicate that the parent substance, *isotrehalose octacetate*, is a β,β form.

Octacetates of the Trehalose Sugars.—The relations which have just been derived among the rotations of the three trehaloses and the α and β forms of glucose apply likewise to the fully acetylated derivatives of these five substances. Thus the molecular rotation of α,β -trehalose octacetate may be regarded equal to the sum of the molecular rotations of the α and β glucose pentacetates, which is known to be +41400, and its specific rotation (mol. wt. 678) in chloroform is calculated to be +61. The observed specific rotation of pure trehalose octacetate in chloroform is +162 (Hudson and Johnson, *Journ. Am. Chem. Soc.*, 1915, xxxvii., 2752), which indicates again that trehalose is the α,α form. The specific rotation of the β,β form, or *isotrehalose octacetate*, is calculated from these two rotations, by the same method that was used with the sugars, to be -40 in chloroform. Fischer and Delbrück found -17 in benzene, a difference which may be due to the change of solvent, because trehalose octacetate rotates -162 in chloroform and +171 in benzene. (Measured recently in the Carbohydrate Laboratory, Bureau of Chemistry, U.S. Department of Agriculture, by Dr. J. M. Johnson).

Other Compound Sugars of the Trehalose Type.—It may be useful to indicate that the rotation of nearly all the possible sugars of this type may be calculated from existing data. As an illustration consider the tetrasaccharide *lactose* <> *lactose*, a combination which E. Fischer and H. Fischer have sought to prepare through the condensation of bromo-acetyl lactose (*Ber.*, 1910, xliii., 2532). Since the α and β forms of lactose (mol. wt. 342) rotate +86 and +35 respectively, twice the molecular rotation of the lactose chain is +41400. Since the molecular weight of the tetrasaccharide is 666, the specific rotation of its α,β form is calculated to be $41400/666 = +62$. Assuming that the asymmetric lactonyl carbons uniting the glucose residues have the same rotations that were found for them in trehalose, $2A' = +44000$, and hence the specific rotation of the α,α form of the tetrasaccharide is calculated to be $(41400 + 44000)/666 = +128$, and that of the β,β form $(41400 - 44000)/666 = -4$.

From the specific rotations of the α and β lactose octacetates (mol. wt. 678), +54 and -4 in chloroform (Hudson and Johnson, *Journ. Am. Chem. Soc.*, 1915, xxxvii., 1273), and the value +68500 for the two lactonyl carbons (calculated as in the case of the trehalose octacetates), the specific rotation of the fully acetylated derivatives (mol. wt. 1255) of *lactose* <> *lactose* may be calculated to be, for the α,β form $+33900/1255 = +27$, for the α,α form $(33900 + 68500)/1255 = +82$, for the β,β form -28. The similar derivatives of maltose and cellose can be treated in the same way. The calculations are here indicated because the work of E. Fischer and H. Fischer, and Zemlen (*Ber.*, 1910, xliii., 2536) appear to open a way for synthesising these compounds of lactose, maltose, and cellose, respectively, when sufficient material is available.

Lastly, the expected specific rotation of β,β -arabinose <> β,β -arabinose (mol. wt. 282) may be calculated from the specific rotations of the α and β forms of the sugar, +76

* From the *Journal of the American Chemical Society*, xxxviii., No. 8.

and +184 respectively, to be $(76 + 184)150 + 44000/282 = +294^\circ$. (The assigning of a positive rather than negative sign to 44000 (= 2A), although the compound is a β -derivative, is made because the arabinose is the levo form. (See *Journ. Am. Chem. Soc.*, 1909, xxxi., 72). This rotation is of interest because it appears to be the largest specific rotation that can be expected among the sugars from present data.

The Related Rotations of Lactose and Cellose.

There are three disaccharides which have the general structure $\text{glucose} < \text{glucose} <$, namely, maltose, cellose, and gentiobiose, and two of the composition $\text{galactose} < \text{glucose} <$, namely, melibiose and lactose. In these structures the place of attachment of the left-hand glucose or galactose molecule is evidently its lactonyl carbon, but several points of union for the right-hand glucose molecule are possible. Without more knowledge of this point of attachment for each of the compound sugars, it does not seem possible in general to obtain relations among their rotatory powers. However, there is one special case which can be adequately treated at present, and it leads to an interesting relation between the rotations of lactose and cellose. The structures shown above indicate that for each point of attachment in the right-hand glucoside residue, there can be four related sugars according as the left-hand member is α - or β -glucose, or α - or β -galactose. To formulate the rotations of these forms let G and Ga, respectively, be the rotations of the left-hand glucose and galactose chains, L that of their bound lactonyl carbons, and R that of the common right-hand glucose residue. Since the free lactonyl group of this residue permits α and β forms, let R refer throughout to the same one of these. The molecular rotations of the four structures are thus:—

$$\begin{aligned}\alpha \text{ Galactose} < \text{glucose} < \dots &= \text{Ga} + \text{L} + \text{R} \\ \alpha \text{ Glucose} < \text{glucose} < \dots &= \text{G} + \text{L} + \text{R}\end{aligned}$$

$$\text{Difference} \dots \dots \text{Ga} - \text{G}$$

$$\begin{aligned}\beta \text{ Galactose} < \text{glucose} < \dots &= \text{Ga} - \text{L} + \text{R} \\ \beta \text{ Glucose} < \text{glucose} < \dots &= \text{G} - \text{L} + \text{R}\end{aligned}$$

$$\text{Difference} \dots \dots \text{Ga} - \text{G}$$

The differences are equal to each other, and as will be seen readily are also equal to the difference of the molecular rotations of the corresponding α and β forms of galactose and glucose, or of methyl galactoside and methyl glucoside. We reach the conclusion therefore that if either of the $\text{galactose} < \text{glucose} <$ sugars (melibiose or lactose) has a structure in which the right-hand glucose residue is identical with the similar component of one of the $\text{glucose} < \text{glucose} <$ sugars (maltose, cellose, or gentiobiose) the pair of sugars, in case both are α -glucosidic compounds or both β , should differ in molecular rotation by the difference between the molecular rotations of the galactose and glucose chains. The difference in specific rotation of β -methyl galactoside (0°) and β -methyl glucoside (-32°) (of mol. wt. 194) is $+32^\circ$, which amounts to $(32)194/342 = +18^\circ$ in the specific rotation of the disaccharides (mol. wt. 342). If $+18^\circ$ be added to the specific rotation of the β forms of maltose ($+118^\circ$) (Hudson and Yanovsky, forthcoming publication) and of gentiobiose (-11°) the sums $+136$ and $+7$ do not agree with the rotations of either β -melibiose ($+124^\circ$) or β -lactose ($+35^\circ$). On the other hand, the rotation of β -cellose ($+16^\circ$) $+18^\circ$ is equal to that of β -lactose (35) almost exactly.

The Rotations of the Octacetates of these Sugars.—It is highly desirable to test in independent ways this conclusion that lactose and cellose have the same structure for their common glucose residue, and that the galactose residue of one belongs to the same series (probably the β , judging from the low rotation of lactose) as the glucosidic glucose residue of the other. If the similarity does exist

it would be expected to extend to many derivatives of these sugars, and it should be possible to decide from a comparison of the rotations of each pair of derivatives whether the agreement that has been found to hold for the parent sugars is a general one and really has for its basis the assigned reason, or is an accidental agreement in the one case tested. The rotations in chloroform solution of the pure octacetates of the disaccharides in question are known, and a comparison of them appears to be of special value because in them the rotations of the individual asymmetric carbon atoms in the glucose residue are doubtless quite different from the values for the sugars themselves. The difference between the specific rotations of tetraacetyl β -methyl galactoside (-13°), of mol. wt. 362, and the corresponding acetylated β -methyl glucoside (-18°) (Hudson and Dale, *Journ. Am. Chem. Soc.*, 1915, xxxvii., 1265) is $+5^\circ$, which corresponds to $(5)(362)/678 = 3^\circ$ for the disaccharide octacetates. The addition of this value to the specific rotation of β -maltose octacetate ($+63^\circ$) gives a sum entirely different from the rotation of the β -octacetate of either melibiose ($+102^\circ$) or lactose (-4°). On the other hand, the rotations of the β -octacetates of both cellose (-15°) and gentiobiose (-5°) yields sums (-12 and -2°) which are near the rotation of β -lactose octacetate (-4°). The combination of this result with that obtained from the rotations of the sugars themselves, in which gentiobiose was clearly ruled out, gives strong evidence that the common glucose residues of lactose and cellose have identical structure.

THE TRANSFORMATION OF NITRILES INTO AMIDES BY HYDROGEN PEROXIDE.

By L. McMASTER and F. B. LANGRECK.

THE first use made of hydrogen peroxide as a hydrolytic agent for converting nitriles into amides was by Radziszewski (*Ber.*, 1885, xviii., 355). The action takes place according to the equation—



Radziszewski found that the reaction took place easily in the presence of a small amount of alkali and at a temperature of about 40° . He was of the opinion that it would proceed especially well in all cases where the amide formed is insoluble in water, and gave as examples the formation of benzamide from benzonitrile and capronamide from capronitrile. Radziszewski used a 3 per cent solution of hydrogen peroxide.

Deinert (*Journ. Prakt. Chem.*, 1895, [2], liii., 431) applied this method to different nitriles, and obtained very fair yields of the corresponding amides from benzonitrile and *p*-tolunitrile, poor yields from benzylcyanide and benzonaphthene nitrile, very poor yields from propionitrile and alphanaphthene nitrile, and no yield at all from *o*-tolunitrile. He thus came to the conclusion that the nitriles gave different results according to their constitution.

Bogert and Hand (*Journ. Am. Chem. Soc.*, 1902, xxiv., 1034) used this same method for the direct formation of quinazolines from *o*-acylaminobenzonitriles, and Bogert and his associates have frequently used the same method since.

Keiser and McMaster made use of this method to convert fumarnitrile into fumaramide (*Journ. Am. Chem.*, 1913, xlix., 81). Practically a quantitative yield was obtained.

In October, 1915, we began a more thorough study of this method to see whether it could not be made of wider application and better yields obtained, particularly by the use of more concentrated solutions of hydrogen peroxide than had been previously used. Deinert used 1.8, 2.5,

and 8.0 per cent solutions, but found that the 2.5 per cent solution was the best one to use. We have applied our modification of the method to the transformation of benzonitrile, *m*-nitrobenzonitrile, *o*-tolunitrile, *p*-tolunitrile, alpha-naphthonitrile, beta-naphthonitrile, terephthalnitrile, trichloroacetonitrile, and isobutylacetonitrile into the corresponding amides. Recent abstracts give an account of some recent work by Dubsy (*Fourn. Prakt. Chem.*, 1916, [2], xciii., 137) on the transformation of nitriles into amides by the Radziszewski method. Dubsy has brought about the hydrolysis of several nitriles into amides by using a large excess of a 3 per cent solution of hydrogen peroxide. He was thus able to convert *o*-tolunitrile and alpha-naphthonitrile into amides, whereas Deinert found that they remained practically unchanged when treated with the usual amount of hydrogen peroxide.

We have been unable to obtain the original article of Dubsy's, and since we have worked with two of the same nitriles mentioned in the abstracts, and found that the same results were obtained by using concentrated solutions of the peroxide instead of a large excess of the usual 3 per cent solution, and since we have applied the method to a larger number of cases than Dubsy has, we thought that we should publish our results already obtained with the nitriles mentioned above. We also intend to apply the method in the case of many other nitriles.

Experimental.

Benzonitrile.—5 grms. of benzonitrile were added to 50 cc. of a 6 per cent solution of hydrogen peroxide, and the mixture made slightly alkaline with sodium hydroxide. The mixture was stirred at a rather high rate of speed by means of a motor-driven apparatus to insure an intimate mixture of the substances. The temperature of the mixture was kept at 65° for 1.5 hours, during which time the amide separated out as white flakes. The stirring was now interrupted and the mixture surrounded by ice and salt, whereupon more of the amide separated. It was filtered off, washed with cold water, dried over sulphuric acid for forty-eight hours, and crystallised from absolute ethyl alcohol. The yield was about 92 per cent of the theory. M.p. 128°. The m.p. recorded in the literature is 128° (Schiff and Tassinari, *Ber.*, 1877, x., 1785).

Calculated for $C_6H_5CONH_2$ —11.59 per cent; found—11.50 per cent N.

***m*-Nitrobenzonitrile.**—1 gm. of *m*-nitrobenzonitrile was added to 15 cc. of an approximately 20 per cent solution of hydrogen peroxide, the mixture made slightly alkaline, and warmed to 65°. The mixture was shaken vigorously, placed in the dark, and allowed to stand, with occasional shaking, for twenty-four hours. At the end of one hour a thin layer of white crystals formed at the surface of contact of the hydrogen peroxide solution and the nitrile which floated on the surface. The solution became a bright yellow-green in colour. At the end of twenty-four hours the pale yellow crystals, which had separated and fallen to the bottom of the tube, were filtered off, washed with cold water, and dried on a suction filter. The crystals were dissolved in a minimum amount of hot absolute ethyl alcohol, and the amide freed from any unchanged nitrile by suddenly cooling the hot alcoholic solution in a freezing mixture. The nitrile, being less soluble than the amide in the alcohol, crystallised out first, and was filtered off. On allowing the alcohol to evaporate the amide crystallised out. This process was repeated several times until a product of m.p. 141° was finally obtained. The recorded m.p. of *m*-nitrobenzamide is 140–142° (Reichenbach and Beilstein, *Ann.*, 1864, cxxii., 141). The final recrystallisation yielded beautiful white needles, some of which were 4 cm. in length. The crystals of the amide formed were rather difficultly soluble in ethyl alcohol, ether, benzene, petroleum ether, and water. The yield obtained was 80 per cent of the theory.

Calculated for $C_6H_4(NO_2)CONH_2$ —16.87 per cent; found—16.97 per cent N.

***o*-Tolunitrile.**—Deinert (*loc. cit.*) could not transform this nitrile into the corresponding amide by the use of hydrogen peroxide. Dubsy (*loc. cit.*) found that 2.5 grms. of the nitrile in 50 cc. of methyl alcohol gave a yield of 2.1 grms. of *o*-toluamide on treatment at 40–60° with 200 cc. of 3 per cent hydrogen peroxide and 10 cc. of N sodium hydroxide, the reaction product being neutralised, evaporated to dryness, and extracted with alcohol.

We added 10 cc. of a 15 per cent hydrogen peroxide solution to 1.1 grms. of the nitrile in a large test-tube, and, after making the mixture slightly alkaline, it was warmed to 65° and shaken vigorously. After standing twenty-four hours a white crystalline mass had formed at the surface of the liquid. On warming the mixture again the unchanged nitrile separated from the enclosing crystalline mass. The contents of the tube were again heated to 65°, shaken, and allowed to stand for another twenty-four hours, whereupon more of the amide was formed. On further similar treatment no more amide formed. The crystals were filtered off on a suction filter, dried, and taken up in absolute ethyl alcohol. From the third recrystallisation the amide separated as white semi-transparent needles, readily soluble in ethyl alcohol, moderately soluble in ether, and quite insoluble in cold water. The crystals obtained melted at 138°. Weith found that *o*-toluamide melts at 138° (*Ber.*, 1873, vi., 42). The yield was 90 per cent of the theory.

Calculated for $C_6H_4(CH_3)CONH_2$ —10.37 per cent; found—10.42 per cent N.

***p*-Tolunitrile.**—Deinert obtained from 2 grms. of this nitrile, dissolved in alcohol, 2 grms. of amide (instead of 2.3 grms.) which melted at 155°. We added 1 gm. of the nitrile to 10 cc. of a 15 per cent solution of hydrogen peroxide, made the mixture slightly alkaline, and warmed it to 60°. The nitrile melted to a yellow oil. After shaking the mixture for some time it was allowed to stand for twenty-four hours. The amide was filtered off, dried, and crystallised from absolute ethyl alcohol. The crystals melted at 155°.

The experiment was repeated by treating 2 grms. of the nitrile with 50 cc. of a 10 per cent hydrogen peroxide solution and warming the mixture to 60°. Instead of shaking the mixture we stirred it for one hour, at the end of which time the reaction was complete. The voluminous flaky mass of amide on the surface of the liquid was filtered off, washed with water, dried, and crystallised from ethyl alcohol. The crystals were found to melt at 155°. The literature records various melting-points for *p*-toluamide. Fischli gives 151° (*Ibid.*, 1879, xii., 615), Gatterman and Schmidt give 156° (*Ann.*, 1888, ccxlv., 51), while Holleman gives 158–159° (*Rec. Trav. Chim.*, vi., 78). Deinert records 155° (*loc. cit.*). The amide is described as fine needles when crystallised from alcohol (Fischli) or large plates when crystallised from water (Gatterman and Schmidt). We obtained monoclinic needles of about 5 mm. in length. The yield obtained was about 90 per cent of the theoretical.

Calculated for $C_6H_4(CH_3)CONH_2$ —10.37 per cent; found—10.30 per cent N.

***α*-Naphthonitrile.**—Deinert observed practically no change in this nitrile when treated with hydrogen peroxide. Dubsy was able to convert it into amide by means of a large excess of the reagent, but the abstracts of the article above referred to do not state the amount obtained. By treating 1 gm. of the nitrile with 20 cc. of 10 per cent hydrogen peroxide and making the mixture slightly alkaline, we were able to obtain a 20 per cent yield after allowing the mixture to stand one week with occasional shaking and warming. The mass which formed was filtered off, washed with cold water, and placed on a

porous plate. It contained some unchanged nitrile which would probably have changed to the amide had we continued to add hydrogen peroxide and allowed the mixture to stand longer. The porous plate was placed in a water-oven and warmed to 45°. The greater portion of the unchanged nitrile (m.p. 36°) was absorbed by the plate, and the amide remained as white crystalline flakes. The amide was then freed from the remaining traces of nitrile by refluxing the mixture with a very small amount of ethyl alcohol and suddenly cooling it. The amide, being less soluble in alcohol than the nitrile, separates first, and can be filtered off. The amide, recrystallised from alcohol, melted at 202°. The literature records 202° as the m.p. of alpha-naphthoamide (Hofmann, *Comptes Rendus*, 1868, lvi., 476; Leone, *Gazz. Chim. Ital.*, 1914, xiv., 122).

Calculated for $C_{10}H_7CONH_2$ —8.18 per cent; found—8.16 per cent N.

β -Naphthonitrile.—1 grm. of beta-naphthonitrile was added to 25 cc. of 10 per cent hydrogen peroxide solution, the mixture made alkaline, and warmed to 70°. The mixture was shaken vigorously, and then allowed to stand. At the end of one hour fine white needles began to form. The hydrogen peroxide decomposed very rapidly, and the solution became bright yellow in colour, later changing to bright red and finally to brown. Hydrogen peroxide was added from time to time, and after twenty-four hours the transformation seemed to be complete. The solid mass which had formed was filtered off and washed, first with water and then with alcohol to remove any unchanged nitrile. The amide is difficultly soluble in alcohol and remained on the filter. It was, however, recrystallised from alcohol, and allowed to stand over sulphuric acid. Small rhombohedral plates of m.p. 192—193° resulted. There was a slight sublimation during the determination of the melting-point. Vieth and Leone record 192° as the melting-point of beta-naphthoamide (*Gazz. Chim. Ital.*, xiv., 123).

Calculated for $C_{10}H_7CONH_2$ —8.18 per cent; found—8.27 per cent N.

From 2 grms. of beta- $C_{10}H_7CN$ Deinet. obtained 0.8 grm. of beta- $C_{10}H_7CONH_2$ instead of the calculated amount, 1.12 grms. From 1 grm. of the nitrile we obtained 0.9 grm. of the amide.

Terephthalnitrile.—The dicyanide of terephthalic acid, purified from boiling alcohol, was treated with hydrogen peroxide solution and a small amount of alkali. The mixture was warmed to 40°, and a vigorous action took place. A white amorphous compound, with a yellowish tinge, formed. This was separated from any unchanged nitrile by boiling alcohol in which the nitrile is soluble, while the amide is insoluble. Terephthalamide is insoluble in all ordinary solvents (de la Rue and Müller, *Ann.*, 1862, cxxi., 90). We found our product to be insoluble in all such solvents. The compound, thus prepared, melted above 250°, and gave off ammonia when treated with potassium hydroxide solution. The yield was not determined.

Calculated for $C_6H_4(CONH_2)_2$ —17.07 per cent; found—17.10 per cent N.

The amide was then boiled with alcoholic potassium hydroxide until ammonia was no longer evolved (ten hours). The alcohol was allowed to evaporate spontaneously, leaving the white salt of terephthalic acid. The salt thus formed was dissolved in water, and treated with dilute hydrochloric acid, but not enough to neutralise the solution, for the free acid, which would form, is difficultly soluble in water. A concentrated solution of barium chloride was now added to the solution, and also more hydrochloric acid to make the mixture more nearly neutral. White barium terephthalate formed, which was washed on a suction filter and dried at 150—160° for two days.

Calculated for $C_6H_4(CO_2)_2Ba$ —45.58 per cent; found—45.52 per cent Ba.

It was thus proved that we had prepared the pure terephthalamide from the nitrile.

Trichloroacetonitrile.—2 grms. of trichloroacetonitrile were added to 40 cc. of 3 per cent hydrogen peroxide solution. The mixture was treated with a few drops of sodium hydroxide solution and stirred at a high rate of speed for five minutes. An energetic action took place, and some free chlorine was liberated. The mixture was then set aside in the dark. At the end of two hours a few fine white needles had separated, but at the end of twenty-four hours a mass of white needles, some of which were 2 cm. in length, had separated. These were filtered off, washed with water and then with 50 per cent alcohol. The nitrile is very soluble in alcohol, while the amide is only fairly soluble in this solvent. The needle-like crystals of the amide were recrystallised from cold alcohol and placed over sulphuric acid for one week. They melted at 137°. Zincke records the m.p. as 141° (*Ber.*, 1901, xxxiii., 241).

Calculated for CCl_3CONH_2 —8.62 per cent; found—8.55 per cent N.

From 2 grms. of the nitrile we obtained 0.9 grm. of the amide.

Isobutylacetonitrile.—1 grm. of the nitrile was added to 50 cc. of 3 per cent hydrogen peroxide solution, the mixture made very slightly alkaline, and stirred at a high rate of speed for one hour, the temperature being maintained at 20°. It was found in preliminary experiments that a 6 per cent, or stronger, solution of hydrogen peroxide caused oxidation to isocaproic acid, and the presence of even 2 or 3 cc. of a 10 per cent solution of sodium hydroxide brought about the same result. The alkalinity of the solution continually tended to disappear, and frequent additions of a drop of sodium hydroxide solution were necessary. At the end of one hour the stirring was interrupted and the mixture allowed to stand twenty-four hours. The mixture was then cooled to 10°, when a small amount of precipitate formed. This was filtered off and crystallised from alcohol. M.p. 121°. The filtrate was evaporated to dryness on the water-bath, and the residue taken up in hot absolute alcohol. On cooling the alcoholic solution flaky crystals of isobutylacetamide formed. This process was repeated several times. The crystals melted at 121°, with a slight sublimation at 118.5°. The recorded m.p. is 120°. The yield was about 70 per cent of the theory.

Calculated for $(CH_3)_2CH(CH_2)_2CONH_2$ —12.17 per cent; found—12.22 per cent N.

Conclusions.

1. We have thus prepared nine amides in the pure condition from the corresponding nitriles. Their analyses (for nitrogen) have been made and some of their properties studied.

2. We have found that some of the nitriles, which formerly could not be transformed into amides by the ordinary concentration of hydrogen peroxide, can be transformed by more concentrated solutions of the peroxide.

3. It has been shown that the change of nitriles into corresponding amides by hydrogen peroxide, under stated conditions, is a generally applicable method.—*Journal of the American Chemical Society*, xxxix., No. 1.

Society of Chemical Industry.—The Council meetings arranged for Friday, March 23, and Wednesday, May 23, will, in order to suit the convenience of the President, be held on Thursday, March 22, and Tuesday, May 22, respectively, at 2.30 p.m. Owing to the difficulty in obtaining good films in the present dull weather, the lecture on "Commercial Aeronautics," by Mr. Holt Thomas, announced for March 21st, has been postponed until May 20th. Mr. M. A. S. Riach, will deliver his paper on "Air Screws" on March 21st.

CLEAN CULTIVATION OF POTATOES.*

By SAMPSON MORGAN.

Failure of the Scientists.

UNDER clean culture, food reform means pure and natural food for earth, plants, and trees, as well as men. At the present time, though the food stocks may suffice in spite of the submarine peril, nevertheless, if my plan of operations—which I have outlined each year in ample time for utilisation since the first day of the war—had been adopted our granaries would have been full and running over with an abundance of true foodstuffs, and the whole population would have been enjoying the blessings of the fivepenny and sixpenny 4 lb. loaf, and potatoes at equally tempting prices. Although a change has been made at the Department of Agriculture, it is evident that, with slight alterations, the old out-of-date methods are to be continued. Mr. Prothero certainly does not possess that practical knowledge which is essential; and this his plans prove, for he has failed to act as generously with the farmers of Britain as the situation deserved, and as the result the prospect is far from promising. With the enemy at our gates, threatening us with a curtailment of food supplies, the time for soft words is past. A bounty on every acre of wheat, barley, oats, and potatoes especially, would have brought forth an abundance of these health-giving foodstuffs, and the fixing of a maximum instead of a minimum price for wheat and potatoes was an error. The nation which has its granaries full to overflowing is the nation that can stand out the longest in this titanic conflict, in which the British, with their allies, are fighting against barbaric foes who would blast the hopes of humanity and trample right and justice under foot if they could.

The strength of Germany, as I have pointed out in my clean culture pamphlets, is mainly due to the magnificent manner in which it has for some years fostered rural industries. In Britain, for fifty years the peasants have been divorced from the soil. In Germany the contribution of the agricultural workers was equal to that of her city merchants. Here the national physique has declined, as the large number of Army medical rejections prove.

Despite the increased attention paid in Germany to agriculture, the effect of the teachings of the scientists, agricultural chemists, and experimenters has been, as in Britain, of a harmful nature. I am aware that such a sweeping statement may be read with astonishment by many, but the fact remains. The productive power of the German acre is less than that of the British acre, and the productive power of the latter, mainly because of false science teaching, is 50 per cent less than what, at a moderate estimate, it should be. The reason for this is simple enough. These teachers have not gained their experience upon the land. Book and laboratory learning are all very well in their way, but they cannot make up for lack of practical training.

Disease Proof Potatoes.

Last year over half a million tons of potatoes were lost through disease. At £8 a ton the producers were poorer by £4,000,000, and the national granary was depleted seriously at a time when it could least afford a shortage. The potato is one of our best foodstuffs, for the acre output is considerably higher than that of the grain. Potato disease has caused the cultivators the loss of countless millions of money during the past fifty years. At the present time the stamina of most of our potatoes is at a very low ebb. Disease resisting potatoes are not abundant, despite the study which scientists and experimental station expert have devoted to that affection. They have failed to give us the disease proof potato, and I insist that so long as they work on the old unscientific and stereotyped lines they never will. Seasons, temperatures, and soil conditions have something to do with it I admit, but so

they have with human ailments. Still, if those conditions which favour disease were absent, nevertheless it would remain, for the simple reason that as man is what his food makes him, so plants are what their food makes them. In the health compact with nature, food is the essence of the contract. No one can treat it as a scrap of paper without paying the penalty—and in full.

Soils are poisoned by the carbonate of ammonia in manure, the excessive and continued use of which on farms for years is the cause of soil sourness, and with the latter present perfect fertility is impossible. I was the first writer on soil dietetics to explain the cause of soil sourness in glasshouses. I proved beyond question that the failure of peaches to hold and perfect their fruits, which so freely fell prematurely from their trees, was due to the continued use of manure—that is, farmyard manure. In a paper before me a writer suggests—"Farmers must still regard farmyard manure as the basis of fertility." On another page another writer says—"Owing to the continued use of manure many soils of market gardens are seriously declining in fertility." Still in the same paper, a third writes—"Poultry manure poisons plants." The thousand correspondents who some years back I circularised on this subject all agreed that their crops on farms and in gardens were unsatisfactory, although they had been users of manure for years.

Astonished at my denunciation of manures, a well-known and large fruit grower and farmer near Sittingbourne once wrote me, saying—"I am quite nonplussed at your clean culture teaching, for we farmers have been brought up to believe that manure is the sheet anchor of agriculture, and that when manure fails we should turn to chemicals." But that belief was shattered when I pointed out that the main value of manure was in its humus-making properties, and, as chemicals contained none of them, it was not possible for the one to take the place of the other.

There is only one way to annihilate potato disease, and that is by feeding disease-resisting qualities into the potato. This is sense and science. Year after year so-called disease resisting potatoes have been announced, and they run out one after the other in doleful succession.

Breeding may be Important, but Feeding is much more so.

If potatoes are improperly fed they will in time, however strong their constitutions at the start, run out and degenerate. So long as manure is looked upon as the sheet anchor of agriculture, so long will potato disease, blights, poor crops, and sour soils be the plague of the farmer. I may be told that the officials at the Department of Agriculture, our agricultural chemists, County Council lecturers, trade magazine writers, and others all boom manure, and surely there must be some grounds for these united commendations.

Scandalously Neglected Acres.

But the fact remains that in the majority of cases the acre averages are most unsatisfactory, and the major part of the land is imperfectly and improperly cultivated. There are hundreds of thousands of acres of land in the country which are practically left to themselves from one year's end to the other, nothing being fed to them except waste animal manure from grazing stock, with the result that these pastures are impoverished, and produce grass of such a weak and watery nature as to be unfitted to furnish health-giving food to the cattle which range about them. The milk from cows kept on such pasture is of most questionable quality, so that from every point of view a radical change is imperatively necessary.

Within my time scores of new fertilisers have been trotted out, supported with glowing testimonials from chemists and scientists, but they have left the scene for good, and others crop up almost daily. It is the same in the United States, where, after spending millions on such each year for forty years, not an ounce has been added to the acre output of the crops they were fed to, despite the costly nature of these so-called plant foods.

* From *The Vegetarian*, March, 1917.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, March 1, 1917.

Sir J. J. THOMSON, O.M., President, in the Chair.

PAPERS were read as follows:—

"*A Graphical Method of Drawing Trajectories for High Angle Fire.*" By Prof. W. E. DALBY, F.R.S.

Last session I communicated a paper (*Proc. Roy. Soc., A*, cxii., 239) explaining a graphical method of finding the range, time of flight, angle of elevation, and other elements of a trajectory, from the data given by a curve showing the resistance of a standard shell in terms of the velocity. The graphical method followed the analytical method laid down in the military text-books. The paper dealt with direct fire, which is officially defined as "fire under angle of elevation 150° ."

The present paper is a continuation of the paper referred to above, adapting the graphical method to high angle fire. For this the density of the atmosphere has to be brought into the calculation as one of the variables of the problem. Briefly, the method consists in applying the graphical method explained in my first paper in a series of steps, dealing in each step first with the vertical element of the trajectory and then with the corresponding horizontal element of the trajectory.

The magnitude of a step is so selected that the influence of the change of tenuity on the resistance is negligibly small during the part of the trajectory corresponding to the step. The value of a quantity corresponding to, but not the same as, the ballistic coefficient in direct fire, is changed from step to step to allow for the changing value of the tenuity as the shot moves in its trajectory.

The method is applied to determine the trajectory of a shell weighing 380 lbs., fired from a 9.2-inch gun elevated to 40° , taking the conditions of the shots fired during the Jubilee Trials in 1898.

"*Osmotic Pressures derived from Vapour Pressure Measurements. Aqueous Solutions of Cane-sugar and Methyl Glucoside.*" By The EARL OF BERKELEY, F.R.S., E. G. J. HARTLEY, and C. V. BURTON.

The paper forms a continuation of researches on the same subject already communicated to the Society. If the ratio of the vapour pressure of a pure solvent to the vapour pressure of a solution is known, the osmotic pressure between the solution and the solvent can be theoretically calculated. Since the osmotic pressure is proportional to the logarithm of the ratio of the vapour pressures, a specially accurate determination of the value of the ratio is required in order to obtain good values for the osmotic pressure. The paper deals with the experimental arrangements for determining the vapour densities and the special precautions that have been taken to secure a high degree of accuracy. A number of corrections applicable to the simple theoretical formula have been examined, both experimentally and theoretically. The experimental results given refer to solutions of different degrees of concentration. The dissolved substances dealt with are cane-sugar and methyl glucoside and sulphuric acid, while the solvent in each case is water. The experiments were made at standard temperatures of 0° C. and 30° C.

"*The Complete Photo electric Emission from the Alloy of Sodium and Potassium.*" By W. WILSON.

The subject of this investigation is the law governing the variation of the complete photo electric emission with the temperature of the source of full radiation causing it.

Theoretical considerations indicate that this law should be the same as that governing the temperature variation of the thermionic emission from hot bodies, namely, that expressed by the formula—

$$C = AT^{\frac{1}{2}} e^{-\frac{\phi}{2T}};$$

In the main, most of the troubles in this connection are due to the teachings of Liebig, Gilbert, and Lawes, all of whom reaped golden harvests through introducing and commending artificials. Our Department of Agriculture have followed in the footsteps of these men, and have glorified their unscientific teachings. Why?

If one-third of the scandalously neglected acres of farm land were properly cultivated this year we could add ten million tons of the most perfect foodstuffs to the coming harvest. Again, last autumn the Department of Agriculture neglected in the most criminal manner to assure a greatly increased crop of winter wheat. There is ample time for the production of bumper harvests of barley, oats, and potatoes this year. We may increase the potato output at a low estimate by 2,500,000 tons. The national acre output is under seven tons. It could be made ten. That would mean an increased provision of 3,750,000 tons. They have been grown to produce over a gallon a root, equal to fifty tons an acre, but then this crop was obtained under clean culture, the method which bans manure as a poison.

A Lincolnshire grower recently wrote me saying, "I never could get anything like a crop of onions until I heard of and tried clean culture, then for the first time I got wonderful crops, and what wonderful keepers the onions were!" Scores of similar testimonials have reached me from all parts of Britain.

Internal Nutrients and Sugar.

Under clean culture wheat, barley, oats, and potatoes may be grown to perfection, and the internal nutrient quality of each will be enhanced considerably, the wheat being as rich in albuminoids as the best hard Durum, or macaroni wheat. In the same way the sugar percentage of all fruits may be increased remarkably. If the farmers want sugary swedes and mangels let them cultivate their crops on clean culture lines. As to sugar beets, nothing the whole of the scientists combined can furnish will feed sugar into sugar-beets in any way comparable to clean culture ash-fertilisation, which latter the Department of Agriculture and Rothamstead have been compelled to endorse, though without acknowledgment. What is wanted is a greatly increased acre average output of roots, fruits, and grains, and a greatly increased sugar or nutrient percentage at a much cheaper cost for fertilisation than is possible with chemicals or artificials, and nothing but clean culture can do the business.

The starvation white loaf has gone, the semi-starvation "Standard" loaf has also gone, the War loaf remains, and this is the next best to the loaf made from flour with 100 per cent of the grain. But when we get that in general use we must go a step further; the perfect loaf can only be made from the perfect grain, and the perfect grain can only be produced by clean culture fertilisation, which enables the plant to elaborate perfectly healthy internal tissue.

A well-known food reformer recently wrote:—"Your work is of first national importance." Two important lectures are to be delivered in the Midlands shortly on the wonders of clean culture. At last the country is waking up to the value of my work in respect to the development of the nation's acres, which I have persistently carried on for over half a life-time.

To be continued.

Mineral Products of the United States in 1915.—The value of the mineral production of the United States in 1915, according to preliminary figures compiled by the United States Geological Survey, was approximately 2,373,000,000 do's., a gain of 258,000,000 do's., or more than 12 per cent over 1914. The value for 1915 has been exceeded but once—in 1913—when a total of 2,439,000,000 do's. was recorded.—*Chemical Engineer and Manufacturer*, xxiv., No. 5.

where T is now the temperature of the source of radiation, C is the photo-electric current per unit area of the emitting substance, A and ϕ are characteristic of the substance and independent of T , and λ is a small number, probably not differing much from 2.

Experiments are described in which the alloy of sodium and potassium was exposed to approximately full radiation. A wide range of photo-electric currents and the corresponding temperatures of the radiator were measured, and the relation between them was found to be well expressed by the above formula.

SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS.

Ordinary Meeting, March 7, 1917.

Dr. H. G. COLMAN, Vice-President, in the Chair.

A CERTIFICATE was read for the second time in favour of Mr. Hubert Charles Siegfried de Whalley.

Prof. Alfred Francis Joseph, D.Sc., F.I.C., was elected a member of the Society.

The following papers were read:—

"The Quantitative Estimation of Mercury in Organic Compounds." By J. E. MARSH and O. G. LYE.

"Composition of Milk." By P. S. ARUP, H. C. HUISS, and H. DROOP RICHMOND.

The average composition of milk for 1914-1916 is given in the accompanying table.

Year.	Sp. gr.	Total solids.	Fat.	Solids not fat.
1914	1.0317	12.52	3.72	8.80
1915	1.0319	12.62	3.76	8.86
1916	1.0318	12.67	3.82	8.85

Attention is drawn to the fact that there is less difference than formerly between the fat in the a.m. and p.m. means, being 0.25 in 1914, 0.18 in 1915, 0.24 in 1916. A study of the distribution of the fat percentages leads to the conclusion that the morning milk in 1914 can only be expressed as a mixture of two kinds of milk—one of p.m. quality and the other of a quality containing 0.4 per cent less fat—and the average deviations from the mean of these two qualities, as well as the difference between them, agree with those formerly deduced when the average difference actually was 0.41.

The case of Hunt v. Richardson was discussed, and it was pointed out that, in order to comply with this judgment, it was necessary that great care must be taken to prove that no alteration of composition by natural means has occurred.

"Studies in Steam Distillation." By H. DROOP RICHMOND.

PART IV. *Propionic, Butyric, Valeric, and Caproic Acids.*—Descriptions of the methods of purifying the acids used are given, and distillations of aqueous solutions of each in fractions lead to the following values of the rate of distillation:—

	Calc.
Formic acid.. ..	0.4013 + 0.0256 log 100 S
Acetic acid	0.678 + 0.013 "
Propionic acid ..	1.224 + 0.0222 "
Butyric acid	2.00 — "
Valeric acid	3.50 "
Di-ethyl acetic ..	4.75 (for $n=4.5$)

The formula used for calculation was $a = 0.4013 \times 1.72 n$, where n is the value in $C_nH_{2n+1}COOH$.

PART V. *Some Applications of Duclaux's Method.*—The application of the above constants to the analysis of acetic anhydride, acetyl chloride, acetyl salicylic acid, and substituted malonic acids is discussed. Incidentally, the

method of Menshutkin and Wasiljew for acetic anhydride, which appears to have been overlooked, is referred to, and the slight volatility of salicylic acid (rate = 0.107) and its influence on the analysis discussed.

"Note on Salvarsan and Neo-salvarsan." By JOHN WEBSTER.

NOTICES OF BOOKS.

Theoretical Chemistry from the Standpoint of Avogadro's Rule and Thermodynamics. By Prof. WALTER NERNST, Ph.D. Revised in accordance with the Seventh German Edition by H. T. TIZARD, M.A. London: Macmillan and Co., Ltd. 1916. Pp. xix+853. Price 15s. net.

THE fourth English edition of this work has been prepared from the seventh German edition, which differed materially from its predecessors. A great quantity of new material was added, and although no development of physical chemistry is neglected in the book special prominence is given to those branches which have been the subjects of Prof. Nernst's own work. Of these the treatise gives a complete review, and it is particularly valuable for its treatment of modern theories. The translation has been thoroughly well performed, and the printing is so good that it appears invidious to call attention to a slip on page 509 ("cyrohydrate").

The Oxford Museum and its Founders. By A. VERNON HARCOURT, Hon.D.Sc., F.R.S.

THIS pamphlet gives an account of the foundation of the Oxford Museum, and incidentally discusses the attitude of the University towards natural science fifty years ago. Part of the author's Presidential Address to the Chemical Section at the Bristol meeting of the British Association in 1875 is reprinted, and also a letter to *The Times* on compulsory Greek, in which the arguments for and against its retention are admirably put.

Empire Trade Notes. No. 1, January, 1917.

THESE notes are to be published monthly by the British Empire Producers' Organisation, whose purpose is to stimulate Empire trade development. The subjects briefly discussed in the first number include the manufacture of glass bottles, the production of steel in this country (which it is estimated will by the end of the war be double what it was in 1914), the margarine industry, flour export and the war, &c. These notes will help to keep the manufacturer and trader informed as to the resources and commerce of the British Empire, and the Organisation is undoubtedly doing useful work in stimulating trade within the Empire.

MEETINGS FOR THE WEEK.

MONDAY, 19th.—Royal Society of Arts, 4.30. (Aldred Lecture).

"Memorials and Monuments," by L. Weaver.

TUESDAY, 20th.—Royal Institution, 3. "Geological War Problems,"

by Prof. J. W. Gregory.

Institution of Petroleum Technologists, 8. "Sulphur in Petroleum Oils," by F. Mollwo Perkin.

WEDNESDAY, 21st.—Royal Society of Arts, 4.30. "Colour Printing and some Recent Developments," by G. W. Jones.

Microscopical, 8. "Bacteriology of War Wounds," by Dr. Kenneth Goadby.

THURSDAY, 22nd.—Royal Institution, 3. "Modern Improvements in Telegraphy and Telephony—Telegraphy," by Prof. J. A. Fleming.

Royal Society. "Observations and Experiments on the Susceptibility and Immunity of Rats towards Jensen's Rat Sarcoma," by J. C. Mottram and S. Küss.

FRIDAY, 23rd.—Royal Institution, 5.30. "Magic in Names," by Edward Clodd.

SATURDAY, 24th.—Royal Institution, 3. "Russian Idealism—The Russian Madonna," by Stephen Graham.

THE CHEMICAL NEWS

VOL. CXV., No. 2391.

THE TRAINING AND WORK OF THE ENGINEERING CHEMIST.*

By Sir ROBERT HADFIELD, D.Sc., F.R.S.

It is with great pleasure I rise to offer a few words of introduction with regard to this important and representative gathering which meets in order to consider the question of the training of the engineering chemist, who, it can be said, covers such a wide ground of work. There is no doubt that each important and major branch of industry demands its own special type of chemist. In other words, as an example, a chemist who is well trained and suitable for the chemical industry would probably not shine as a chemist in the industry of ferrous metallurgy. This naturally comes about through the type of work to be carried out being entirely different. It is evident, therefore, that no one course of training can cover all the requisite ground.

As an illustration of the points of difference prevailing between the various lines of work, may I point out the following:—

The Ferrous-Metallurgist in one of the branches of his work has mainly to deal with temperatures and combinations which occur far above those relating to the ordinary chemical industry. We Ferrous-Metallurgists are every day dealing with metals and combinations of metals requiring temperatures of from 1400°C . to 1600°C . as regards the metals themselves in their molten condition. The temperatures required to bring about this molten condition is of still higher order, probably up to 2000°C ., or to the steel maker using electric furnaces temperatures considerably over 3000°C .. Even in the lower ranges of temperature, such as used during rolling, forging, heat treatment and other operations, temperatures are far higher. For example, rails are rolled at from, say, 1100°C . or 1200°C ., and many other instances can be quoted. Even then our work is not done. We have to deal with the same metals at quite another set of temperatures known as "treatment temperatures," varying from 500°C . to 900°C ., and, finally, in some cases when tempering still another and lower set of temperatures are met with. In all these we want the guidance, care, and knowledge of the engineering chemist and physicist.

The Non-Ferrous Metallurgist, on the other hand, steps down considerably in the average temperatures he uses for fusion, rolling, forging, and other operations, thus requiring another type of experience and training.

The foregoing are only used as illustrations; similar facts are met with, too, all along the line of industrial chemistry. Consequently, therefore, it may rightly be said that it is not practicable, nor should it be proposed that, whilst there must be common ground on basic facts relating to the training of our engineering chemist, no one routine training will cover all these requirements. Does not this in itself seem to indicate that somewhat early in his training the student should more or less branch off into specially studying the particular lines of work with which he expects to be associated during his working career?

I will not enter into the domains of chemical industry outside these special lines with which I am familiar, because in them I do not pretend to be proficient. We shall this

evening have most able papers from those who have made a life study of the subject as a whole and in detail.

Speaking personally, my early training as an engineering chemist, as far as I can recollect this, seems to have occurred something on the following lines, which my hearers, humorous as they may regard the circumstances, may take as quite correct.

My earliest impression appears to hover around Brewer's "Guide to Science," followed by that really admirable work known as "Pepper's Playbook of Science," which, to my own mind, had in its day great influence in stimulating interest in Science. So much have I felt indebted to that work that not long ago, after its being re-written, with additions by Mr. John Mastin, M.A., in 1913, and republished by Routledge, I had the pleasure of presenting several hundred copies to the various Board Schools in Sheffield, and understand they have been appreciated and found of service.

My first actual experiment, so far as I can remember, and after no doubt reading the wonders, as they then seemed to be, set forth in the books I have mentioned, related to some experiments in producing a temperature sufficiently low to freeze an ice-cream mixture. For some reason which I cannot now fathom, the freezing mixture, which contained some H_2SO_4 , was placed in a porous jar, probably because it was "handy." Consequently, I nearly poisoned myself, and numerous friends gathered together to share in the wonders of modern chemistry as applied to the production of ice-cream of a superior low temperature palatable to that portion of the genus homo known as "boy."

A second example related to what may be termed a more advanced type of scientific work, that is to the production not this time of low but high temperatures by means of a Fletcher gas furnace, in which at home I was trying in a privileged corner of the cellar to melt a few ounces of steel. I remember how hard I worked with the foot blower, and what expenditure of energy was required to keep the blower going! It is really no mean feat to raise and maintain a temperature of "some dimensions" approaching 1600°C .. The cellar was no doubt selected because of its propinquity to the fuel, and where a tiresome experimentalist might be allowed to work in apparent safety, as it was thought that beyond spreading somewhat noxious fumes in the house no harm could happen. Nevertheless, the final result was that I succeeded in starting a fire that nearly burnt down the house!

Did these famous personal records, instructive as no doubt they were to myself, represent chemical training misapplied? No! I venture to say that it was "Better to have loved and risked experiments than never to have experimented at all."

To return to our subject. We are this evening fortunate enough to have with us many of our leading chemists, and in the introductory Address by Sir George Bailby, F.R.S., to the general discussion on the "Training and Work of the Chemical Engineer," or, as Professor Dinnan, I think, rightly prefers to call it, "The Engineering Chemist," and of which I have had the pleasure of seeing an advance copy, we have wise words from one of our greatest living chemists. In his comparatively recent honour of Knighthood we offer our most hearty felicitations, and as a recognition that men of scientific attainment are not forgotten in the Honours List.

Sir George will, from his point of view, deal with the functions and training of the Engineering Chemist and Engineering Chemistry, so I need not go further than say sound schemes which add to and increase the efficiency of our chemists are most desirable. My own feeling is that, in some respects, a successful chemist of the first rank is born and not made. It is most desirable that increased facilities should be given to training our young and rising chemists after the war. No doubt, owing to the sad losses which are prevailing in our midst, there will be much shortage in labour, whether mental or physical, of the highest class. We cannot therefore do too much to

* Remarks by the President to the General Discussion on "The Training and Work of the Engineering Chemist," held by the Faraday Society, March 6, 1917.

set our house in order now, and that those whose duties and age do not call them to run the terrible risks and hardships of our brave fighting men at the front should, with might and main, be planning wisely and well improvements and additions to our curriculum of scientific training to meet those conditions which are sure to arise after the war.

It has been said that we are not a scientific race; on the other hand, the world has derived probably more benefit and made greater advances from the discoveries of the British chemist than through any other race of men. I refer any "doubting Thomas" to the very able lecture, entitled "English and German Methods Contrasted," given before the Royal Society of Arts by my friend, Dr. Dugald Clerk, F.R.S.

It is not necessary to mention names of British chemists of modern times, but I venture to maintain that, although we admit our enemy on the Continent has paid great attention to the training of the chemist, he has paid not less attention to the absorption of basic British ideas, which have enabled him to arrive at the position he has done in the past, aided as our enemies there have been by the fostering care of a paternal Government.

When dealing with Engineering Chemistry it would seem reasonable to say a word with reference to the State organisation of Scientific Research. A very interesting report has recently been presented by Mr. G. Lightfoot, M.A., F.R.S., to the Parliament of the Commonwealth of Australia, and we know what has been done here by the Advisory Council for Scientific and Industrial Research, on the Council of which Sir George Beilby, who is with us to-night, is a member. In view of the excellent report by Mr. Lightfoot as regards the Commonwealth, it would be interesting to know on what new lines our Advisory Council for Scientific and Industrial Research is going to proceed in the near future. Are they going to distribute the large sums we hear of, running into seven or eight figures, or are these rumours in the realms of fancy only? At any rate, we wish them God-speed in their efforts to spread and encourage research. That this country is not so much behind, in other words, we are not as black as we have been painted, was, I think, evidenced by the fact that Professor George E. Hale, of the National Research Council, who is taking up this matter in America, came over to this country, rather than to the Continent, to learn "How to do it."

It is true we Anglo-Saxons, whether on this side or the other side of the Atlantic, are largely individualists; but by co-ordination and co-operation there is no doubt we can greatly improve our world's work, and still maintain the immense advantages of individualism, which, after all, is honest and straightforward. It has not tried to invade neighbouring small countries whose neutrality was guaranteed, and crush out their existence by the foulest possible means.

As regards one class of Research, Americans can certainly teach us something; for it appears that, in the year 1914, there were sixty-nine Agricultural Colleges, their endowment value of buildings and stock amounting to the large sum of thirty-two million pounds, with an annual income of seven million pounds. No less than 69,000 students were instructed by something like 6000 instructors.

The Bureau of Standards, with its different sections, deals with (a) Electricity, (b) Weights and Measures, (c) Heat and Thermometry, (d) Chemistry, (e) Structure of Materials, (f) Engineering Research, (g) Metallurgy, and its annual expenditure is about £125,000—a model, indeed, of wise expenditure on behalf of the Nation's needs.

There is no greater field for research than in the science of Chemistry, and I trust that some of the papers which are to be read this evening will add increased zest to our efforts in this direction, and open new veins of thought which are before us in the great domain of Nature.

In addition to the opening Address by Sir George Beilby, we have papers this evening from Professor F. G. Donnan,

F.R.S., on "The Training of the Chemical Student for Work in the Factory"; by Mr. Charles R. Darling, on "The Training of the Works Chemist in Physics"; Mr. W. R. Cooper, M.A., B.Sc., on "A Plea for the Forgotten Factor in Chemical Training"; and Mr. J. W. Hinchley, on "The Work of the Imperial College in the Training of Chemical Engineers."

We are also to have present with us, and contribute to the discussion, Mr. C. S. Albright, Dr. E. F. Armstrong, Dr. Charles Carpenter, Dr. Dugald Clerk, F.R.S.; Professor E. G. Coker, F.R.S., Mr. S. Z. de Ferranti, Mr. A. P. M. Fleming, Mr. E. Hatschek, Professor G. G. Henderson, Professor A. K. Huntington, Mr. H. A. Kent, Mr. W. McNab, Dr. R. Messel, F.R.S., Sir Gerrard Muntz, Bart., Dr. F. M. Perkin, Mr. K. B. Quinan, Mr. W. Gathorne Young, and others.

The Faraday Society, whether as regards its President or members of Council, believe in trying to see a thing through in the same evening; so, if we sit until a late hour, I trust this will be agreeable to those present. The subject is so important that an extra half an-hour or an hour, even in these times, can safely be spared. If it is not possible to get through the discussion in one evening, I suggest that the meeting be adjourned to a future date.

Finally, there is one matter to which I should like to refer this evening, specially as what I am going to say intimately concerns the main subject which we have gathered together to discuss. As we all know, this country not long ago sustained a great loss in the death of our eminent chemist, Sir William Ramsay. As a mark of respect to one of our most honoured amongst chemists, I suggest that we all rise.

Reference to this honoured man gives me the opportunity of saying what I hope will be considered as a few apposite words regarding the Ramsay Memorial Fund, which has an intimate relation to the subject of our discussion to-night. The work is being taken up by a strong Committee, upon which I have the honour of representing our Society.

I attended a meeting of the Executive a few days ago, at which Sir Hugh Bell presided as Chairman, amongst others present being Lord Rayleigh, Sir William Tilden, Mr. Scott (President of the Chemical Society), Sir William Mather (President of the British Science Guild), Prof. F. G. Donnan, Prof. J. Norman Collie, and others.

Not only this country, but the world generally, suffered a great loss by the death of Sir William Ramsay, who occupied one of the highest positions as a scientific investigator and discoverer in the science of chemistry, and as you are aware, this Ramsay Memorial Fund is to be founded as a memorial of his great work.

A Meeting was held at the University College on October 31, 1916, under the Chairmanship of Lord Rayleigh, and was attended by representatives not only of our own Government, but also of the leading neutral Powers and the principal Scientific Societies of Great Britain and Ireland. The Postmaster-General proposed a resolution, seconded by the President of the Royal Society (Sir Joseph J. Thompson), supported by His Excellency the Belgian Minister and by the American Ambassador, that a Memorial Fund should be formed to be utilised for the purpose of promoting chemical training and research, under a scheme to be hereafter approved by the supporters. An appeal is to be made before long to invite subscriptions to this Fund from all friends and admirers of Sir William Ramsay throughout the world, so that it will be cosmopolitan.

I refer to this matter to-night, because amongst the objects the Executive Committee will have in view will be the provision of Ramsay Research Fellowships, and the establishment of a Ramsay Memorial Laboratory for dealing with the special subject we are this evening discussing, namely, "Engineering Chemistry." I specially draw your attention to the use of this term because it is one which is suggested by one of our most able chemists, Prof. F. G. Donnan, F.R.S., from whom this evening we

are to have the pleasure of a paper. I must confess that I have myself often been puzzled by the loose use of this term "Chemical Engineering," and I think the new one proposed, "Engineering Chemistry," far better describes that phase of chemical knowledge now to be discussed; I trust with advantage, not only to those who are present, but those who will afterwards follow our Proceedings through the Press and through our Journal.

Let all those who are present spread the knowledge that a bold attempt to launch this important Ramsay Fund is being made. The object in view is indeed worthy of the attempt. If it is said that the present is a bad time; shall a country which has just raised a loan of a thousand million pounds fail to provide just recognition of the work of one of the ablest chemists of modern times, and of whom every Englishman is proud? We are often apt to look back and think of the work of such men as Newton, Cavendish, Lavoisier, Faraday, and other great men, forgetting that in modern times we have had with us such a man as this great chemist, the Englishman, Ramsay, whose name has probably stood highest in chemistry throughout the world.

Let us therefore this evening not only have in mind the many interesting papers and subjects brought before us, but also remember that there could have been no greater pleasure and satisfaction given to this great patriotic Englishman who has passed away from our midst than to know that in his honour and his memory we, who are at the present time struggling amidst vicissitudes of all kinds, find time and opportunity to keep flying the flag of science, and thus honour his memory by perpetuating his great life work, in the proposed Ramsay Memorial Fund. Before long, full information will be given to those who are desirous to assist, so I will not add anything further to these remarks at the present time.

NOTE ON THE COLOURING MATTER OF RED TORULAE.

By ALFRED CHASTON CHAPMAN.

SOME years ago I undertook in conjunction with Mr. F. G. S. Baker, an investigation of the red *torulae* with the object of isolating as many distinct species as possible, and of obtaining results which might serve as a basis of classification. In connection with this work, during which six different species were obtained and studied, I commenced a subsidiary investigation of the red colouring matter present in these organisms.

One of the six species of *torulae* above referred to was grown on large plates containing wort-agar. When a sufficient quantity had accumulated the growth was scraped off, care being taken to remove as little of the agar surface as possible. It was then dried at a low temperature and was thoroughly ground with fine sand. The resulting material was then extracted with various solvents, chloroform and carbon disulphide giving the best results. In the case of both these solvents deep red solutions were obtained, which on cautious evaporation gave a coloured residue containing fat and probably some phytosterol. With the small quantities obtained the separation of these fatty substances was found to be impossible, and consequently no crystals could be got. It was found at the commencement of the work that the solution in chloroform when warmed and exposed to the light quickly became colourless, a fact which suggested that the colouring matter might be allied to carotene. The extracted substance behaved like carotene in certain other respects, being practically insoluble in water, and dissolving in concentrated sulphuric acid with a deep blue colour. About the time the work had reached this stage, Schimon presented to the University of Munich, a dissertation

dealing with certain red coloured lower fungi. He appears to have obtained the same general reactions for the extracted colouring matter, and concluded that it was identical with carotene. Prior to the publication of this dissertation, I had commenced a study of the absorption spectrum of the colouring matter, with the object of comparing it with that of carotene, and I observed that the two were not by any means the same. The examination was first made in carbon disulphide solution, with a glass prism, and the spectra were photographed, using Wratten and Wainwright's "Panchromatic" plates. In the case of the colouring matter from the *torula*, the light passed between wave lengths 5900 to about 7000, whilst in the case of carotene, a much larger amount of the yellow portion of the spectrum was visible, the range of wave lengths being from about 5500 to 7000. In view of these results, I decided to make an examination of the colouring matter with a quartz prism, so as to obtain some information in regard to the far violet. The source of light used consisted of a Nernst lamp, and the solution of the colouring matter was contained in a Baly tube permitting of a progressive increase in the thickness of the solution examined without changing the containing vessel. For each exposure the position of the sodium lines was recorded by means of a small reflecting prism attached to the instrument, and on each plate the copper arc was photographed as an additional aid to fixing the position of the bands. Solutions of pure carotene (prepared from carrots) in carbon disulphide were compared side by side with corresponding solutions of the *torula* colouring matter. In both cases observations were made in thicknesses 1, 2, 3, 4, 5, 6, 8, 10, 13, 16, 20, 25, 32, 40, 50, and 63 mm. The strength of the carotene solution was 5.3 mgrms. per litre, and the solution of the *torula* colouring matter was made of such a strength that the intensity of the absorption bands was comparable with that of the carotene bands. Wratten and Wainwright's "Allochrome" plates were used, as these are insensitive to red light of greater wave length than about 5890. These, however, show a thin absorption band in the green, due to the colouring matter used in the preparation of the plates. "Panchromatic" plates were found to be less suitable for the purpose. The resulting spectrographs were found to differ very considerably and in a manner which might have been anticipated from a consideration of the absorption spectra as observed with the glass prism. It was found that in the case of the colouring matter of the *torula*, practically the whole of the yellow is cut off in solutions of sufficient concentration, whereas even in very much stronger solutions of carotene the whole of the yellow passes. Moreover the absorption band in the blue is much wider in the case of carotene than in the case of the *torula* colouring matter.

It is clear from these observations, either that the colouring matter of the *torula* consists of some other substance than carotene, or that it consists of a mixture of carotene with some other colouring matter. The solubility of the *torula* colouring matter in light petroleum appears to indicate that it does not belong to the xanthophyll group.

My best thanks are due to Dr. Monier-Williams and to my assistant, Mr. Frederick T. Harry, for valuable help in connection with the preparation of the spectrographs.—*Biochemical Journal*, x., No. 4.

Huggins' Memorial.—On Thursday next, March 29, at 3 p.m., Sir J. J. Thomson, the President of the Royal Society, will unveil the Memorial to Sir William and Lady Huggins in St. Paul's Cathedral. Addresses will be given by the President and by the President of the Royal Astronomical Society. Admission to the ceremony will be by ticket, and any Fellows who desire to attend should apply without delay to the Assistant Secretary, Royal Society, Burlington House, London, W.

CHEMICAL COMPOSITION VERSUS
ELECTRICAL CONDUCTIVITY.*

By COLIN G. FINK.

SOME years ago, while still at the university, I carried out a number of experiments on the electro thermic production of ultramarine. Powdered mixtures of sodium sulphide, china clay, and carbon were interposed between carbon electrodes in a closed crucible furnace. I observed at the time that in order to keep the electrical resistance and the temperature of the charge fairly low so as to avoid decomposition of the ultramarine as soon as it was formed, it was necessary to use very finely-divided carbon, such as lampblack. With charges made up of powdered coke which was coarse compared to the lampblack, I could not get any appreciable current to pass between the carbon electrodes up to potentials of 250 volts.

Subsequently, I have found repeatedly that the electrical conductivity of mixtures of finely-divided substances is a function of the relative size of the components.

Experimental.

A series of tests was made in order to get values of a more quantitative nature. Two substances were selected, the physical properties of the one as divergent as possible from those of the other; a black metal powder, tungsten, and a white insulator powder, thoria. The advantages in this selection are manifold; both tungsten and thoria will stand very high temperatures, and can therefore be made practically moisture-proof. It is a well known fact that in all high resistance tests adsorbed moisture is a very disturbing factor. Metals such as copper and silver were not serviceable, since they cannot be heated to high temperatures without partial vaporisation, which though slight was sufficient to cover the surface of the insulator granules with a highly conductive film. Other factors that decided our selection in favour of tungsten and thoria were:—(1) High state of purity; (2) availability of both in extremely fine powdered form (readily sifted through 250 mesh gauze); (3) constancy and stability under ordinary atmospheric conditions; (4) sharp distinction in colour; (5) high specific gravities (which reduced the tendency to dust).

All mixtures here recorded were made up of equal weights of tungsten and thoria. As regards the size of the particles, as stated above, the mixtures would pass readily through silk having 250 meshes to the inch. The holes in this silk are about 0.001 in. in diameter. All attempts to segregate particles of a well-defined size by such methods as suspending in water, organic liquids, or air, were frustrated on account of the persistent tendency of the very fine particles to form agglomerates.

We finally resorted to the familiar "tap test." This gave us fairly good comparative values of the fineness of the various powders used. Ten grms. of the powder or powder mixture were filled into a 10 cc. glass graduate and tapped to constant volume; usually, after seven minutes no further decrease in volume could be detected. The ultimate volume in cc. divided by 10 gave us the relative volume (v_r) as recorded in Table I. It can easily be demonstrated that the values for v_r are a function of the density and mean particle size. At first there seemed to be a serious objection to the tap test, namely this, that a powder composed of, say, equal parts of coarse and fine particles would give the same value for v_r as a second powder whose particle size was a mean between the two limiting sizes of the first powder. This objection to the tap test was automatically set aside, since in the ordinary preparation of metal or oxide powders in single small lots by far the greater majority of particles are approximately of the same size. This tendency to form a

"standard" size is a universal phenomenon, the dimensions of any particular standard being dependent upon the physical conditions, such as temperature, strength of solution, &c., under which the particular powder is prepared. (Compare, also, the uniform size of the crystals of granulated sugar as regulated by the strike pan).

TABLE I.
Relative volume (v_r) of—

Mixture.	Mixture.				Appearance of mixture.
	ThO ₂ .	W.	Found.	Calc.	
R	0.720	0.113	0.430	0.417	White
P	0.720	0.350	0.565	0.535	White
Z	0.576	0.235	0.389	0.406	White
T	0.305	0.113	0.200	0.209	White
S	0.305	0.330	0.275	0.318	Black
X	0.238	0.577	0.420	0.408	Black

Referring to Table I., we note that the thoria powders varied in relative fineness between 0.720 and 0.238, and the tungsten powders between 0.577 and 0.113 cu. cm. per gm. The calculated value for v_r of any mixture is equal to one-half the sum of the v_r values of the ThO₂ and W constituents. These calculated values agree fairly well with the experimental, and support our contention that the particles of any freshly prepared powder are of fairly uniform size. If this were not the case no such agreement between the calculated and experimental values would be possible.

As to the appearance of the mixture, if the v_r value for the white powder is high as compared with the value for the black powder, the appearance of the mixture is white; if the white powder is coarser than the black powder, the appearance of the mixture is black. In other words, whenever the ratio of v_r for ThO₂ to v_r for W is greater than 2, the mixture is white; if less than 2 the mixture is black. (The absolute density of W (19.6) divided by the absolute density of ThO₂ (9.8) = 2).

Electrical Measurements.

The powders were pressed into rods of 4 cm. long and 0.5 cm. square. They were then placed in a tungsten hydrogen furnace and fired at 1600–1650° for three hours. This firing caused the rods to sinter together, and rendered them practically proof against moisture. The fired rods were kept in a P₂O₅ desiccator. The rods were then mounted between brass clamps and the resistance measured on a Wheatstone bridge with a sensitive galvanometer. Care was taken to make these measurements on days when the humidity of the air was low. (Compare in this connection H. L. Curtis, "Surface Leakage over Insulators," *Phys. Rev.*, iii., 490).

In view of the differences in "colour" of the various mixtures in the powdered form, it was not very surprising to find marked differences in the electrical resistances although the firing at 1600° resulted in an almost uniform shade for all of the mixtures. In Table II. are recorded four of the characteristic resistance values found. In the last column are the calculated specific resistance values.

TABLE II.

Powder	Resistance	Resistivity
ThO ₂ No. 2.	over 1012 ohms.	over 1012 ohms.
Z	41.8	173.0
X	0.0271	0.108
W No. 1	0.0040	0.016

The powders, ThO₂ No. 2 and W No. 1, were pressed up into rods the same size as those for the mixtures; they were likewise fired at 1600° for three hours.

Since in all of our original powders a small percentage of grains was present whose size was considerably smaller than that of the majority of the grains, the results tend to

* Presented at the 53rd Meeting of the American Chemical Society, New York City, September 25–30, 1916. From the *Journal of Industrial and Engineering Chemistry*, ix., No. 1.

show that under ideal conditions of mixture, relative grain size, uniform distribution, &c., the resistivity values for white mixtures such as Z would be even higher than here recorded. Similarly, the resistivity values for black mixtures such as X would be even lower than those found, approaching a limiting value equal to twice that of the 100 per cent metal rod.

Conclusion.

In general, we may conclude that the electrical conductivity of a substance is primarily dependent upon the shape and the distribution of the fundamental grains or particles composing the substance, and, secondly, upon the presence or absence of thin films of secondary material enveloping these ultimate grains.

On the basis of this theory we can account for the comparatively high conductivity of gels that contain but a trace of conducting material. We can also account for the marked difference in resistance of, say, two samples of commercial copper, whose chemical composition is identical, depending upon whether the impurity, such as sulphur, is uniformly dissolved in the metal, or whether it forms a film ("cement") of copper sulphide around pure granules of copper. The latter case is to be regarded, as Bancroft suggested, as an emulsification of copper in copper sulphide. The high resistance of these surface films composed of, say, sulphide or oxide, or arsenide, accounts for the high resistivity values of copper containing but a trace of one or more of these impurities.

OUR ANALYTICAL CHEMISTRY AND ITS FUTURE.*

By W. F. HILLEBRAND, Ph D.,
Chief Chemist of the Bureau of Standards, Washington, U.S.A.

(Concluded from p. 125).

BEFORE taking up the next phase of my general proposition, it is desirable that the functions which the proposed institution should eventually exercise be clearly understood. At the risk of some repetition I will therefore summarise and for convenience group them under the three heads, Research Work, Referee Work, and Educational Work.

A. Under *Research Work* fall—(a) critical comparison of methods of analysis in use or proposed for different classes of materials in the light of the criteria already presented; (b) improvement of existing methods when possible and devising of new ones if the old are inadequate; (c) recommendation of the methods found to be best suited for commercial needs, accompanied by complete and unambiguous details of procedure together with a statement of the accuracy ordinarily attainable; (d) determination of the causes of disagreement in the results of analysis of the same material by different analysts; and (e) preparation of specifications for reagents.

B. *Referee Work* covers—(a) the making of umpire analyses in cases of irreconcilable disagreement between different analysts; and (b) the preparation and issuing of standard samples for checking methods and the skill of analysts, for volumetric analysis, and for the calibration of instruments such as polarimeters and calorimetric bombs.

C. *Educational Work* involves—(a) co-ordination of researches in progress, so that the results when available will be better suited for intercomparison and therefore more useful; (b) assisting in the wider adoption of standards and methods already accepted and found to be satisfactory; (c) study of and recommendations regarding the best methods of teaching analytical chemistry; (d) preparation and publication of bibliographies upon analytical

chemistry; and (e) answering questions of all kinds relating to chemical analysis.

I have purposely refrained from including methods of physical testing, for fear of overstepping the legitimate field of an institution intended for chemical research. However, it might be proper to consider eventually if many methods of physical testing that are ordinarily employed by chemists should not be regarded as falling within the scope of an institution of the kind proposed. In any event it should co-operate in the co-ordination of the results of chemical and physical testing.

At the present time much of the literature published as the result of researches and investigations is of such nature as to make the results of limited value, largely because the investigation was not suitably planned or the results adequately recorded and reported to permit of comparison of one worker's findings with those of others who have preceded him. A permanent body which could obviate such a large amount of wasted effort as is now evidenced would in this field alone accomplish a great good for our science. Many investigators would be glad to avail themselves of its advice and criticism, and in many cases the scientific results put forth from our educational institutions and private laboratories might, through the co-ordinating influence of such a body, be made of greatly increased value.

Let us now consider how such an institution might be brought into being. There occur to me but three ways—(1) through one of the existing scientific bureaux of the Federal Government, preferably and naturally the Bureau of Standards; (2) through endowment and control independent of the Government; and (3) through private endowment under some form of federal trusteeship.

The first and second of these plans have their advantages and disadvantages, which will be now set forth. In favour of the first is the prestige which Governmental support and control would lend. Although on first thought it may not always be easy to see why prestige should attach to the decisions of a bureau of the Government in so much greater degree than to an independent establishment, that it usually does is a fact that has been many times borne in upon me.

The prestige attached to the Government is based on several factors, of which it is not easy to estimate the relative potencies. One is that the National Government represents the interests of all the people, that it is disinterested, having no small group to serve exclusively, that it seeks the welfare of the lowly as well as the exalted, that owing to this sense of responsibility and accountability serious scientific work undertaken by the Government is usually conducted in a manner to command the respect of the scientific world. These two factors have supplemented, perhaps, a third, which is that the people regard the Government as a co-ordinating centre having to do with matters of general concern, so that when the Government speaks it is usually not the opinion of an individual but with the authority of the entire Government and for the entire people. That the public looks up to its Uncle Sam as counsellor and adviser is attested by the innumerable inquiries that come daily in his mail from all parts of the country. The conscientious attention paid to these inquiries has had no small share in moulding public opinion.

The readiness with which all interests co-operate freely with Government agencies is especially marked in co-operative scientific research. As the essence of the proposed institution would be co-operation in fundamental chemical research the Government plan would present a strong case. (A slight disinclination is apparent to full and frank co-operative work where commercial or personal interests are involved. Such unfavourable tendency of private work has resulted in appeals to the Government to take up lines of work where conditions are more favourable).

Evidence that prestige attaches in the minds of chemists, as distinguished from the general public, to statements

* The Chandler Lecture, 1916, delivered before the Columbia University, U.S.A.

issuing from Government institutions is afforded by a very evident tendency toward the use of methods of testing that are employed by the Government. This tendency is particularly manifest with regard to methods that are used for checking up deliveries under specifications. It is true that the desire to copy may not be based always on acknowledged superiority of the Government methods, but rather on the wish to reduce the probability of rejection of deliveries, by use on the part of the manufacturer before delivery of the same method that is to determine the question of acceptance or rejection. However this may be, the result tends to bring about in a very natural way a more general and desirable uniformity of procedure. If this is the effect, it follows as a matter of course that the Government laboratories should be awake always to the importance of maintaining and improving the accuracy of their methods and further that they should be afforded encouragement and every facility to enable them to live up to these requirements.

An additional argument for having this work done at the Bureau of Standards is the help that would come through its facilities in physics. The chemical institution proposed would need to utilise the standardising facilities of the Bureau named for all measuring apparatus and to a considerable extent the optical work would have a material bearing upon chemical work, especially in the newer fields of spectro-chemistry, refractometry, and physico-chemical methods generally. It would seem undesirable to duplicate this expensive equipment if it can be made available for the chemical work under consideration.

It has long been my hope that at the Bureau of Standards we might gradually build up a section which should be the clearing-house in all matters of the kind under discussion. We are frequently asked to settle disputes regarding the content of a given element or compound in a great variety of materials and to give information on all manner of analytical procedures. Our ability to grant such requests has been, however, far too limited from lack of a sufficient number of specially-trained analysts and the inability of those we have to spare the requisite time for such problems. These problems often involve a considerable amount of research, for our aim is not only to determine the true value of the material in question but also to ascertain if possible the causes of the differences reported by others. I regard this latter point as of even greater importance than the former because of its educational value. Under the present conditions of federal support I see little prospect of a full realisation of my hope. The cost of upkeep of such a division would be out of proportion to that of other phases of the Bureau's activities, for its complete realisation would be financially equivalent to establishing a new institution.

Other serious objections to support and control by the Government are—(1) the instability of a work that is dependent on annual Congressional appropriations; (2) the likelihood that at any moment in emergencies the men engaged may be called upon to assist in entirely foreign kinds of work; (3) the restrictions of the Civil Service regulations and the inflexibility of the salaries attaching to all statutory positions. The objections enumerated are very important, for without assurance of permanency and continuity of work the success of such a scheme as I have suggested would be highly problematical and its lasting or even temporary interruption when once established little short of calamitous.

The restrictions under the third objection make it difficult or impossible in the first place to select men for particular kinds of work, or to give timely promotions to deserving men, or even to appoint anyone unless a vacancy happens to exist in the grade for which a desired man is qualified. This lack of flexibility in the appointment of new men and the promotion of old and tried ones is one of the most serious handicaps to efficiency in Government service. These statements are in no way to be taken as condemnatory of the principles for which civil service

stands, for the situation in Government service, even with the limitations stated, is vastly better than it was before the Civil Service Commission was established, when political influence controlled appointments, promotions, and dismissals in no small degree. The particular objection that statutory salaries are inflexible might be met by the provision of a special fund, as has been many times done for other purposes. Such funds are less subject to salary restriction than those called statutory, but Congress has been wont to look upon them with disfavour. The objection that was based on the uncertainty of Congressional appropriations would not hold so much for a separate bureau or establishment as for the supposed case of merger with an existing bureau. This follows from the fact that the effect of Congressional action is far less likely to result in abolishing or even hampering seriously the work as a whole of an established bureau than of one of its divisions.

In favour of independent endowment is the greater stability in a certain sense of an institution so supported and a greater freedom of action and choice of men, offset in a measure by its lower prestige. This latter weakness might hold more during the earlier years of its existence, for under proper guidance there would seem to be no reason why it should not in time merit and obtain much, if not all, that now attaches to institutions fostered by the Government. The greater stability alluded to lies, however, rather in a surer continuity of existence than in certainty that the institution will be able always to fulfil its functions in full measure. In times of stress or through unfortunate investments the income might be much curtailed or even cut off entirely, contingencies which Government establishments may be less concerned about.

There is this to be said further in favour of independent endowment and control, that if the control were in the hands of the technical organisations most concerned chemists would come to regard the institution as more peculiarly their own child, in the growth and performance of which each might take pride but for whose conduct they themselves alone would be responsible. Certainly the time is ripe for chemists to be represented by a national institution which should serve for fundamental work of interest to all chemists the same function that private and industrial laboratories serve for their clients.

A compromise between these radically different suggestions for support and control remains to be considered, namely, through private endowment under some measure of federal control, either of the funds or the work. The Smithsonian Institution is a well-known example of federal administration of a private bequest with control of appointments by the Civil Service Commission. The relation of the Bureau of Mines to its work on radium and some other experimental researches is suggestive of how Government supervision of work might be made compatible with outside control of all expenditures except, perhaps, for the salary of the Government official in charge. If Congress could be persuaded to contribute a building and to locate it on the grounds of the Bureau of Standards, where its staff would be in close touch with men engaged in many fields of testing and research, physical as well as chemical, the conditions might be ideal for attaining the maximum of success. Such juxtaposition might fail in its aim, however, if salaries in the two neighbouring laboratories had no common basis. Stated a little differently this means that salaries for statutory positions under the Government ought to be materially increased, for as already intimated, I regard the payment of adequate compensation as vital to the success of my general proposition.

The kind, degree, and manner of control to be exercised by the Government would need careful consideration, particularly with respect to the choice of the staff, for if with any sort of Government control appointments could be made only through the Civil Service a serious hindrance to successful operation would arise.

Finally, the question must be asked: What is the likelihood of such an establishment ever becoming a realisation? To this no answer is immediately at hand. Certainly nothing will come of the proposal if it does not meet with the approval of the best judgment among chemists, and then still nothing unless a popular sentiment in its favour is awakened, nourished, and made to grow by persistent discussion. The needed impulse and the demand created, the rest should not be so difficult now that we are awakening to the importance of chemistry to the life of the nation. The interests of the great chemical industries, or of industries at whose foundations chemistry lies, could surely be depended upon to create, through endowment or influence upon Congress, an institute for analytical research which would be the first of its kind and which would help to place this country in the very forefront of progress among nations. The industries have received so much from pure science in the past without adequate return that the time seems ripe for them to contribute generously towards its further development, especially along lines which promise so much to themselves as those which I have indicated. It might even be that some private benefactor would arise to do for chemistry what has been so magnificently done for astronomy, terrestrial physics, biology, and the study of the causes and prevention of disease. Given a properly prepared field I do not feel that I am over-optimistic, considering the wave of interest in matters pertaining to chemistry that is sweeping over the country. The preparation of the field should be entrusted to a carefully selected and energetic committee.

I have already intimated that, whatever plan might be adopted, the closest co-operation should be sought and maintained with the industries. Indeed, an advisory board of outsiders should be selected to assist the director in the planning and administration of the scientific work, and the connection of this board with the affairs of the institution should be very real and not nominal. The laboratory itself should be, however, in no way debarred from taking the initiative without reference to the board proposed. Indeed, the laboratory force would often be in far better position to know or learn the weak points in current procedure than any advisory body.

Here let me interject parenthetically a word on a subject that has been far too much neglected by chemists in the past. It seems that now is the time when they should bring pressure to bear to secure that share of official as well as private recognition which is their right by reason of the immense importance of their work to the general welfare. The relative ease with which hundreds of millions of dollars are obtained for military purposes offers a startling contrast to the almost complete indifference of the great scientific interests of the country to Government aid to science. Without raising controversy over the relative value of military and scientific preparedness it is certainly true that if the scientific societies presented their case for Government aid to science with a fraction of the efficiency with which the case for national defence has been prepared, there is scarcely any ideal for such an institution that could not be promptly realised. It is time that chemists entered the field far more than they have done to show how they can contribute to the general welfare and what they need in the way of countenance and support.

It would be going too far afield at this early stage to propose even tentative details for the organisation and conduct of the proposed establishment, which some of you will perhaps recognise as patterned in its objects and scope somewhat after the international institute for chemistry that Prof. Wilhelm Ostwald advocated in great detail a few years ago. (Only after this address was prepared did that of Prof. G. G. Henderson, President of the Chemical Section of the British Association for the Advancement of Science, Newcastle-on-Tyne, 1916, come to my attention. Prof. Henderson's address contains observations and suggestions which parallel in a measure por-

tions of my lecture, although without specific reference to analytical chemistry). Ostwald had in mind an institute of international scope to cover the whole vast domain of chemistry. I propose one of more restricted and only of national scope. What might grow out of a well-established and successful organisation in the United States with respect to international co-operation may be left for the future to determine. World-wide co-operation from the start would be ideal, but even under normal conditions the task would be herculean, as it is at present impossible of accomplishment. Let us therefore proceed with only our own immediate needs in view, in the certainty that if our initiative succeeds others will copy, and that when the time is ripe we may expect to lead in bringing about the broad world co-operation that must eventually come.

RESEARCHES ON QUINAZOLINES.*

A NEW AND SENSITIVE INDICATOR FOR ACIDIMETRY AND ALKALIMETRY, AND FOR THE DETERMINATION OF HYDROGEN-ION CONCENTRATIONS BETWEEN THE LIMITS OF 6 AND 8 ON THE SORESENSE SCALE.

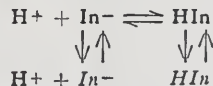
By MARSTON TAYLOR BOGERT and GEORGE SCATCHARD

Introductory.

(NOTE.—Sørensen's system of expressing hydrogen-ion concentration has been used throughout, the "Index" (P_H) being the negative common logarithm of the concentration of hydrogen-ion; i.e., the negative exponent of the power to which 10 must be raised to express this concentration (Sørensen, *Comptes Rendus Laboratoire de Carlsberg*, 1909, viii.; Fales and Nelson, *Journ. Am. Chem. Soc.*, 1915, xxxvii., 2771). Thus, the index 6 represents a hydrogen-ion concentration of 10^{-6} , and 8 of 10^{-8} . This provides a single unit for expressing acidity and alkalinity, and one which can be measured directly by the use of the hydrogen electrode. Further, it is the relative and not the absolute change in hydrogen-ion concentration which affects both the electro-motive force of the hydrogen electrode and the colour of the indicator).

As a means of measuring hydrogen-ion concentration, the use of an indicator possesses the obvious advantage of convenience of operation, practically instantaneous readings and inexpensive apparatus.

Ostwald's explanation ("Wissenschaftliche Grundlagen der Analytischen Chemie," 1901, p. 117) of indicator action as due to an equilibrium between an ion of one colour and an un-ionised molecule of another colour (or colourless), has been quite generally abandoned in favour of the theory that an equilibrium exists between the two forms in both states (Stieglitz, *Journ. Am. Chem. Soc.*, 1903, xxv., 1112; A. A. Noyes, *Ibid.*, 1910, xxxii., 816).



Yet, for a satisfactory indicator, just those conditions are necessary which approximate Ostwald's simple hypothesis so closely as to permit the application of the dilution law to them as to a simple dissociation. That is, for a two-colour indicator, one tautomer must predominate in the ion and the other in an un-ionised molecule; while for a one-colour indicator the coloured form must be absent in one state. In either case the equilibria between tautomers must be unaffected by external factors. With these conditions fulfilled we may then ignore all but the predominating forms.

* From the *Journal of the American Chemical Society*, xxxviii., No. 8.

For a monobasic acid indicator (In.H), the following relation will therefore hold :—

$$(H^+) = K(In.H)/In^-;$$

and for a mon-acid basic indicator (In.OH),—

$$(H^+) = K_w/(OH^-) = K_w(In^+)/K_B(In.OH).$$

An indicator base may therefore be regarded as an acid with $K_A = K_w/K_B$.

We have omitted the term γ for the degree of ionisation of the salt which Noyes uses in his equations, because its use assumes that the equilibrium between the tautomers in the un-ionised salt is the same as in the ion, and that the other ion which goes to make up the salt exists in the solution in the same concentration as the indicator ion. The second condition is seldom even approximately realised in practice, the first we do not know about. Since the error introduced by assuming $\gamma = 1$ is small compared to that made by the other approximations, it does not seem worth while to use the very much more complicated form demanded by the exact expression.

For polybasic acid, or poly-acid bases, the relations are more complex, but probably even then a single colour change is affected by only one ionisation, and the above relation holds at least approximately, which is all that is required for qualitative purposes.

By the depth of colour of a one-colour indicator, or the tint of a two-colour one, the ratio of ionised to un-ionised indicator is measured, and thus the hydrogen-ion concentration. Although theoretically this ratio should vary with the change of hydrogen-ion concentration throughout the whole possible range, there is for every indicator a definite limited region within which this change of concentration is determinable by the colour change. Outside this region either the small amount of one colour is masked by the large amount of the other, in the case of two-colour indicators; or, for one-colour indicators, the amount of colour is too minute to be visible, or too deep for the recognition of a slight change. The range of usefulness hence varies with the different indicators, but is usually one or two units of index. The location of this particular region of serviceability, depending as it does upon the ionisation constants, naturally differs for different indicators. The location and extent of the serviceable range, and the accuracy of measurement, depend upon the amount of indicator required to give visible colour. In general, one colour indicators have wider ranges than two-colour ones, because of the masking of one colour by preponderating amounts of the other, as already pointed out, and they give more accurate readings because it is easier to estimate depth of colour than change of tint.

In titrations where the purpose in using an indicator is merely to determine when a certain definite concentration of hydrogen-ion has been reached, the great advantage of a one-colour indicator arises from the fact that the easiest of all colour changes to detect is the first appearance of colour in a colourless solution.

The accuracy of an indicator is impaired by any factors which cause a variation in the equilibrium between the tautomers. Certain substances affect the colour change by disturbing the equilibrium without changing the concentration of hydrogen-ion. Neutral salts affect most indicators and are particularly troublesome with those of the rosaniline series. Certain organic solvents, like alcohol, likewise often exert a disturbing influence.

Since the use of indicators for determining hydrogen-ion concentration is frequently resorted to in the case of biological liquids, the interfering factors in such solutions are of especial interest, notably the proteins and the commonly used preservatives. The effect of proteins is quite likely due to their colloidal nature, and becomes more serious as the molecular weight and complexity of the indicator increase, being most noticeable with azo indicators of congo-red type. On the other hand, the disturbing action of the ordinary preservatives, such as

chloroform and toluene, is usually due to extraction of the indicator, and those most seriously affected are the basic azo indicators.

Another factor to be reckoned with is the colour of solution to be titrated. This difficulty may be partially remedied by giving the standard the same colour, but it cannot be wholly overcome. For example, a yellow solution would impair but little the usefulness of phenolphthalein, but it would make trouble with methyl-orange, and might preclude entirely the use of *p*-nitrophenol; the disturbance caused by a pink solution, on the other hand, would increase in just the opposite direction.

Still another matter of importance is the permanence of an indicator colour, particularly on standing exposed to ordinary daylight. Some indicators, like hematoxylin, run through a rapid series of colour changes which make them unsuitable for measuring hydrogen-ion concentration; others fade on account of the precipitation of the indicator; practically all lose their colour on long standing in strong daylight. This fading may be so slow that the standards can be used for several days after they have been made up, or it may be so rapid that the indicator must be added at practically the same instant to the solutions which are to be compared.

For many titrations an indicator must be used changing near a fixed point, because of the effect of the hydrolysis of the salt formed upon the hydrogen-ion concentration, and the common ion effect of the salt upon the acid or base. Except near this point the change in hydrogen-ion concentration for a given amount of acid or base added is very slow, as is well illustrated by Hildebrandt's measurements with a hydrogen electrode of the hydrogen-ion concentrations at different points in certain titrations (*Journ. Am. Chem. Soc.*, 1913, xxxv., 847). But for the titration of a strong acid with a strong base these influences are so slight that, with a proper correction for a blank on the water, the indicator may be selected throughout a wide range. In such cases the delicacy is greatly increased when the end-point is near the neutral-point, because the colour change depends upon the relative change in concentration, while the volume added affects the absolute change.

Assuming complete ionisation, it requires 0.009 cc. of 0.01 molar monobasic acid to change the concentration of 100 cc. from an index of 7 to one of 6, while it requires ten times this amount to change it from 6 to 5, and 100 times to change it from 5 to 4. As the range of dinitrobenzoylene urea is from 6 to 8 it is appropriate to consider here other indicators available for this same change.

Azolitmin changes from red to blue with a change of hydrogen-ion concentration from 4.5 to 8.3; but the colour change is too gradual for accurate work, and the indicator is useless in presence of protein.

p-Nitrophenol changes from colourless to greenish yellow from 5 to 7, and is but little affected by outside disturbing factors. Its chief objection is its colour, which renders it unsuitable for use in artificial light or in yellow solutions.

Alizarin changes from yellow to red from 5.5 to 6.8. It is affected by protein and cannot be used in yellow solutions.

Neutral red changes from red to yellow from 6.8 to 8. It is affected by protein, chloroform, or toluene.

Rosolic acid (commercial coralline) changes from yellow to red from 6.8 to 8. The colour change is poor and the indicator is affected by protein.

Cyanine changes from colourless to blue at 7 to 8, but is useless in presence of protein.

Hematoxylin and hematein give too rapid colour changes.

Phenolsulphonaphthalein changes from yellow to reddish violet from 6.50 to 8.50. The effect of salts and protein upon it is now being studied by Lubs and Clark (*Journ. Wash. Acad. Sci.*, 1915, v., 609).

o-Cresolsulphonaphthalein shows the same range and colour change as the last, but its colour change is less

satisfactory. Lubs and Clark are studying the action of protein and salts upon it.

Bromothymolsulphonaphthalein is also being studied by Lubs and Clark in the same way as to the effect of protein and salts. It shows a colour change from 6 to 7.25 from yellow to blue.

So far as we are informed there is no satisfactory indicator now known covering this range of 6 to 8. Sørensen says of this whole region, "il serait certes désirable de trouver des indicateurs supplémentaires."

The colour change in the case of dinitrobenzoylene urea is from colourless to greenish yellow, the colour developing regularly with the change in hydrogen-ion concentration from 6 to 8. This colour change closely resembles that of *p*-nitrophenol, possesses the same advantage as a one-colour indicator, and the same disadvantage due to its colour being yellow. This is of interest, as the compound is structurally more closely allied to *p*-nitrophenol than to any of the other indicators cited, since it may also be regarded as of nitrophenol type. It is but slightly affected by neutral salts and not at all by chloroform or toluene.

Sørensen found that egg albumen was the most troublesome of all proteins with indicators, but that it did not affect *p*-nitrophenol. Comparative tests with egg albumen showed that dinitrobenzoylene urea is no more disturbed by it than is *p*-nitrophenol. The colour of this new indicator fades but slowly. In phosphate solutions it did not fade appreciably in two days, and but very slightly in a week. (The primary and secondary alkaline phosphate solutions used throughout were prepared as described by Sørensen, *i.e.*, were 1/15 molar).

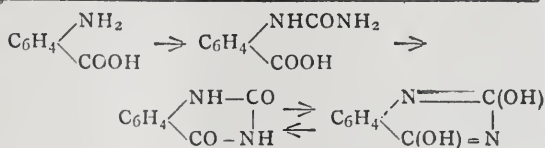
Thus, it would appear preferable to rosolic acid (coralline) for the preparation of neutral ammonium citrate solutions for fertiliser or soil analyses, since the hydrogen-ion concentration of such solutions lies near the middle of its range, and it is possible to make much more accurate readings with it than with the older indicator.

In titrations the acid side of the end point gave an index of 5.93 and the alkaline side 6.09, as measured by electromotive force determinations with the apparatus described by Fales and Nelson (*Journ. Am. Chem. Soc.*, 1915, xxxvii., 2781). These tests were made on phosphate solutions, as the reduction of the indicator by the hydrogen made it impossible to carry out these E.M.F. measurements in its presence, and because a buffer was necessary to keep the hydrogen-ion concentration constant. The figures recorded correspond to a change in hydrogen-ion concentration of 3.6×10^{-7} , or less than 0.004 cc. of 0.01 molar mono-acid alkali to 100 cc. of solution (assuming ionisation to be complete). In practice the change was obtained with one drop of 0.01 molar NaOH. To give an equally distinct change under similar conditions requires in the case of *p*-nitrophenol 5–6 drops, and for methyl orange 10–12. Titrations of 0.01 molar HCl checked to within 0.1 per cent.

This indicator can be used in hot or cold solutions, and its colour is unaffected by nitrous acid. It gives a sharp end-point with ammonium hydroxide solutions and hydrochloric acid. It can be used with NaOH and acetic acid, but it is impossible to titrate to the first yellow colour. It cannot be employed to titrate carbonates, but the error due to small amounts of CO₂ is negligible.

It gives a second colour change at 11 to 13, when the yellow colour becomes much deeper, but this is too alkaline for most practical purposes. An attempt was made to use this colour change for titrations of boric acid with NaOH, but it proved abortive, partly because the indicator gave a pale yellow colour on the acid side of the end-point, but principally because in such a strongly alkaline solution a small change in index requires a large amount of alkali.

Dinitrobenzoyleneurea is readily prepared from anthranilic acid by converting the latter first into the uramino (ureido) acid, which then easily condenses to benzoylene urea,—



The benzoylene urea is nitrated with sulphuric and nitric acids, yielding a dinitro derivative whose mono-sodium salt is used as the indicator. The location of the two nitro groups has not been definitely determined as yet, although one is quite certainly in position 6. The indicator action may be due solely to keto enolic tautomerism, or the nitro groups also may play a part by pseudo-acid tautomerism themselves. In this connection the second colour change already noted at 11 to 13 is quite possibly due to the ionisation of the second hydrogen.

The study of benzoylene urea and related compounds is being continued, and it is hoped that other serviceable indicators will come to light in the prosecution of the work.

(To be continued).

THE PROTECTION OF THE HEALTH OF MUNITION WORKERS.*

WITH SPECIAL REFERENCE TO THE AIMS AND WORK OF THE HEALTH OF MUNITION WORKERS COMMITTEE.

By EDGAR L. COLLIS, M.B.,
H.M. Medical Inspector of Factories.

THE lecture provided an outline of the problems of modern industrial hygiene as they have presented themselves to the Health of Munition Workers Committee of the Ministry of Munitions.

REASONS FOR THE APPOINTMENT OF THE COMMITTEE.

The sudden and extensive development of munition factories, the gradual lessening of skilled workers (drawn away into the army) and their replacement by women, the increasing demand for munitions (the lack of which might imperil military success), and the risk that these new conditions might lead to an industrial breakdown unless guidance and skilled advice were forthcoming, induced the authorities to appoint a Health of Munition Workers Committee.

THE WORK OF THE COMMITTEE.

Simple Laws of Physiology Formulated for Guidance.

The Committee realised that, if the health and efficiency of the works were to be maintained, it could only be accomplished by having regard to simple laws of physiology, such as the following:—

- (1). Alternation of rest and work must be maintained.
- (2). The efficiency of a worker depends upon a supply of sufficient and nourishing food.
- (3). Suitable light, temperature, fresh air, and protection against disease are necessary to health.
- (4). The physical organisation of a woman, though weaker than that of a man, is more suited to continued effort.
- (5). Human beings must, during immaturity, have shorter periods of activity and longer periods of rest than are required by adults.

The Carrying Out of these Laws.

1. At the beginning of the war it was the rule rather than the exception for work to continue every day of the week. The result was a failure; it being found that the

* Abstract of a Lecture delivered in connection with a course of lectures on "Public Health Problems under War and After War Conditions," at the Royal Institute of Public Health, March 14, 1917.

output was no greater than for six days, while the effect on the workers was deplorable. It was realised that one day's rest out of seven was a necessity, and there remained the question of how the remaining six days were to be divided into periods of work and rest. No data were available on which to base conclusions, but, with the assistance of investigators trained in other fields of scientific research, tentative solutions have been arrived at.

2. At the outbreak of war only a few factories were provided with canteens, but since then, owing to Canteen Committees, there have sprung into existence a large number of industrial canteens. The facilities thus offered for obtaining better food have done much to avert the industrial breakdown so greatly feared, and have proved—what we never sufficiently realised before—that, even from the lowest standpoint, the expenditure of money and time in this direction is amply repaid by increased efficiency.

3. Fresh air is as necessary for the preservation of health as food. This simple fact has apparently not been realised by the architects of factories, where, too often, the welfare of the operative has been subordinated to the housing of the machinery, the result being that, owing to overcrowding and want of light and air, infectious complaints make havoc among the workers, to the serious detriment of output. Other matters dealing with healthy environment which have received attention from the Committee include lighting, the provision of first aid appliances and washing facilities, and the prevention of industrial diseases.

4. The incursion of so many women into industrial life, and the arduous work undertaken by them (especially at a time when the provisions of the Factory Acts, devised for their protection, were necessarily relaxed in the interests of output), brought into existence a position fraught with danger unless special arrangements could be made to cope with it. A solution was found in the establishment of the system of welfare supervision, which has done so much to ameliorate the conditions of factory work for women. It is to be hoped that the success of this movement will lead to its adoption with modifications in the case of men.

5. The question of juvenile employment presented a serious problem, owing to the risk that the demand for labour would lead to the employment of juveniles for too long intervals at a time when housing and travelling accommodation presented special difficulties which shortened even more the period of rest. Much has been done in regard to welfare supervision, but much more remains to be done if the physique and mentality of the nation are to be preserved and improved.

CONCLUSIONS.

Many of those problems under consideration, whether concerning the employment of men, women, or children, have only recently been grappled with, and it is amazing that such a stage of industrial progress should have been reached without any serious attempt to solve them. Had the attempt been made earlier much of the bitter heritage of labour unrest which has descended to us might have been spared. We can only hope that, with the new insight which the war has brought us, better understanding may prevail, and the welfare of the industrial population, upon which the prosperity of the Empire depends, be safeguarded to the utmost of our power.

Catalytic Decomposition of Benzoyl Chloride.—Alph. Mailhe and F. de Godon.—Diphenyl can be conveniently and easily prepared by the hydrogenation of benzoyl chloride over divided nickel or nickel chloride. Also benzoic anhydride can readily be obtained by the decomposition of benzoyl chloride over barium chloride or thorium oxy-chloride, heated to 420–450°C.—*Bull. Soc. Chim.*, xxix.-xx., No. 12.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, March 8, 1917.

Sir J. J. THOMSON, O.M., President, in the Chair.

PAPERS were read as follows:—

"Some Effects of Growth-promoting Substances (Auximones) on the Growth on *Lemna minor* in Culture Solutions." By W. B. BOTTOMLEY.

1. Raw peat when further decomposed by means of aerobic soil organisms—"bacterised peat"—is found to contain certain growth-promoting substances (auximones).

2. *Lemna minor* plants cannot maintain growth for any length of time in culture solutions containing only mineral nutrients.

3. The presence of soluble organic matter is essential for complete growth.

4. The addition to the mineral culture solution of 368 parts per million of organic matter from the water extract of bacterised peat resulted, after six weeks, in a multiplication of the number to twenty times, and an increase in weight to sixty-two times, that of the control plants. The water extract free from humic acid, representing an addition of 97 parts of organic matter per million, gave nine and a-half times the number and twenty-nine times the weight; 32 parts per million from the alcoholic extract gave three and one-third times the number and seven and one-third times the weight; 13 parts per million from the phospho-tungstic fraction gave one and a-half times the number and two and a-half times the weight.

5. The effect of the reduction in amount of auximones with successive fractionation of the bacterised peat was also manifest from the general appearance of the plants. Those in mineral nutrients only, decreased in size week by week and became very unhealthy in appearance, whilst there was a progressive improvement in the appearance of the plants supplied with increasing amounts of auximones. Those receiving the larger amounts retained their normal healthy appearance throughout the experiment and increased in size.

6. The beneficial effect of the auximones was not due to a neutralisation of the toxic substances present in the ordinary distilled water, since comparable results were obtained with conductivity water.

7. An interchange of culture solutions, with and without auximones, showed that the plants are very sensitive to the presence or absence of these substances.

"Some Effects of Growth-promoting Substances (Auximones) on the Soil Organisms concerned in the Nitrogen Cycle." By FLORENCE A. MOCKERIDGE.

Peat which has been further decomposed by the action of certain aerobic soil organisms under suitable conditions (bacterised peat) contains plant growth-promoting substances (auximones).

This investigation deals with the effect of bacterised peat and the various auximone-fractions obtained from it upon the four chief groups of soil bacteria concerned in the nitrogen cycle, *in situ* and in liquid culture.

The addition of bacterised peat to soil increased the rate of nitrogen fixation quite independently of any bacteria contained in the material. This increase was not due to aeration, nor could it be brought about by chemically treated peat. Experiments in liquid culture showed that a water extract of this material greatly increased the nitrogen fixation of *Azotobacter* and of *Bacillus radicola*. An alcoholic extract and the decomposed phospho-tungstic acid and silver-baryta fractions from it were also very effective. Similar results could not be obtained with chemically-prepared soluble humus or with artificial humus.

The accumulation of nitrate in soil containing bacterised peat was greater than that which could be accounted for

by the soluble nitrogen which it contained, and took place more rapidly than in a similar soil provided with an equal amount of soluble nitrogen as ammonium sulphate. Since the water extract of the material was found to be directly nitrifiable, its effect upon the rate of nitrification was not tested, but the auximone-fractions, which were not nitrifiable, greatly increased the rate of nitrification of ammonium sulphate solutions.

The auximone fractions were without effect upon the rate of ammonification in soils and upon the ammoniacal fermentation of urea.

The water extract had no effect upon the rate of denitrification, but the auximone-fractions directly inhibited the process.

The work indicates that certain decomposition products of organic matter stimulate the activities of certain soil bacteria, and appear to play an important part in nitrogen metabolism.

PHYSICAL SOCIETY.

Ordinary Meeting, March 9, 1917.

Prof. C. V. BOYS, F.R.S., President, in the Chair.

A PAPER entitled "To Measure the Pressure in a High Vacuum by Observations of Logarithmic Decrement." By Dr. P. E. SHAW, B.A., D.Sc., was taken as read in the absence of the author.

In experiments on the Newtonian Constant (*Phil. Trans.*, May, 1916) the author used a torsion balance in a vacuum which varied in different cases from 15 mm. to 0.0001 mm. pressure. Before sealing the vessel the pressure was determined by a McLeod gauge. Values of the pressure after sealing off were deduced, in the case of the higher vacua, from observations of the damping of the torsion system.

The formula employed is due to the late Prof. Poynting, and can be expressed in the form—

$$P = 35.6 \frac{I}{saT} \lambda,$$

where I = moment of inertia of suspended system, s = area of surface (supposed plane) which is experiencing the resistance, a = mean distance of plane from centre of rotation, T = period of oscillation, and λ = the observed logarithmic decrement.

A table and curve are given showing the relation between P and λ .

A paper on "A Diffraction Colour Box" was read by Mr. A. W. CLAYDEN, M.A.

The apparatus consists essentially of a very simple concave grating spectroscope, of which the slit and grating are situated at opposite diameters of a circle, the spectrum being formed on the arc of this circle. Two independent arms carry fittings on which may be placed either telescope eyepieces or small electric lamps. With the slit of the instrument illuminated by a suitable source, the eyepieces can be set so that any two desired wave-lengths are in the centres of their respective fields of view. The eyepieces are then replaced by the small lamps (the filaments coinciding with the previous positions of the crosslines), and the grating is observed with a small telescope pointed towards the widened slit: the whole of its surface is seen to be illuminated with a mixture of the two colours on which the eyepieces were originally set.

The "concave grating" employed consists of a Thorpe replica of a Rowland plane grating of 14,475 lines to the inch, mounted with its ruled surface in contact with the surface of a concave mirror of 4 ft. focal length. This forms an admirable substitute for the more expensive concave grating.

The author prefers to state results in terms of the number of oscillations per unit of time.

Observations showed that the smallest change of wave-length which could be recognised by the eye as a change of colour was greater than that which corresponded to a

change of period of 10^{12} vibrations per second, or to a change of one vibration more or less in $1/10^{12}$ second.

DISCUSSION.

Mr. TROTTER asked how the minimum difference of wave-length detectable as colour difference compared with the values obtained by Dr. Edridge-Green.

Mr. T. SMITH said that experiments on the minimum colour difference which the eye could detect were valueless unless the exact conditions under which the experiments were made were stated. For example, the comparison of two colours side by side is materially affected by the presence of a black space between them. In Dr. Edridge-Green's experiments the conditions were not good. The experiments were made somewhat as follows:—While viewing the extreme red end of the spectrum, a shutter is brought down towards the red so as to cut off everything above the region to which the observer would give one distinguishing name, such as deep red. A second shutter was then brought up from the red end to cut off the first patch, and the first shutter moved along the spectrum until the boundary of the next "monochromatic" patch was located. By this means the whole spectrum was divided up into about 25 mono-chromatic patches. It is not difficult to repeat these observations, but if they are compared with measurements made in another way entirely different results are obtained. Lord Rayleigh was able, for instance, to distinguish between the colour of the two sodium lines. He had two spectra, one above the other, the upper one being inverted, so that D_1 and D_2 of one spectrum coincided with D_2 and D_1 of the other. Colour comparisons should always be made from simultaneous observations of the two colours.

Prof. C. V. BOYS said he would like to emphasise Mr. Smith's remarks about the effect of varying conditions on the visual estimates of colour. In the colours of soap films, for instance, this difficulty is met with. Where the thickness is nearly zero the colour is black. As the thickness increases the colours of the first order are successively encountered. Between the blue and yellow there is a tint which can only be described as a bad white. He had long been puzzled as to what this colour was, but had eventually discovered a method of overcoming the deceptive influence of the adjacent colours. Usually these films are traversed by long thin folds. The thickness of the folded film is everywhere three times that of the adjacent unfolded film. Points can be found where this doubtful region between the blue and yellow, occurring on the triple film, can be directly contrasted with the first order white in the adjacent single film. It is then seen to be a very good green. A point which had surprised him in connection with Mr. Clayden's apparatus was that the plane grating, which could not be in actual contact with the mirror except at its edges, nevertheless behaved as if it were in good optical contact.

Dr. W. ECCLES pointed out that the minimum colour difference estimated by Mr. Clayden to be perceptible to the eye, if expressed in the same way as an interval in music, works out as about 1.0013. The tone difference just perceptible to the trained musical ear has been stated to be one seven-hundredth of an octave, which works out as 1.001. It is interesting to observe that the sensitiveness of the eye to pitch differences is, like its sensitiveness to inflow of energy, of the same order as that of the ear.

Mr. CLAYDEN, in reply, said that in making his experiments on the minimum difference of wave-length required to produce a noticeable change of colour he had arranged matters so that by using a reversing or non-reversing eyepiece in the observing telescope one or other colour was uppermost in the field of view. The difference in wave-length was then reduced until it was impossible to say which was which. By this method he could detect a difference of two vibrations per $1/10^{12}$ sec., but at the red and violet ends of the spectrum the detectable difference greatly increased. With regard to the President's last remarks, he had himself been very agreeably surprised to

find that the performance of the grating was so satisfactory.

An arrangement for showing by projection on a screen the coloured fringes exhibited when a Thorpe grating is laid with its ruled face against a plane mirror was shown by Mr. A. W. CLAYDEN.

The light from a small lantern is incident in an approximately parallel beam on the interface of the grating and mirror, which are held together in a wooden framework supported on a stand. The position of the grating mirror combination is adjusted so that the central reflected beam or any one of the diffracted beams is returned just alongside the lantern. The beam passes through a projection lens which focuses the fringes on a distant screen. The fringes thus obtained are very bright, and the simplest apparatus and adjustments suffice for their production.

DISCUSSION.

Dr. R. S. WILLOWS mentioned that Fellows had informed him that these fringes had been described by Barus in the *Philosophical Magazine* (July, 1910, and July, 1911). He understood that they had also been exhibited by Rheinberg at the Optical Convention in 1910. Mr. Clayden's method of exhibiting them by projection would, he thought, be distinctly useful to teachers.

An apparatus for studying the effect of Hertzian Waves on the Heart was exhibited by Prof. W. M. COLEMAN.

A simple pendulum, consisting of a cylindrical brass bob terminating in a pointed wire coaxial with the bob, hangs by a piece of string above one of the terminals of an induction coil, so that in its lowest position the point of the bob is within sparking distance of the terminal and vertically above it. The bob is connected by a piece of flexible wire to the other terminal of the coil. When the pendulum is set oscillating there is a shower of sparks every time the bob passes its lowest position. The frequency of intermittence can be varied by altering the length of the suspension. By adjusting the period of the pendulum nearly to the time of a heart-beat any possible effect on the rate of the beating may be observed.

The condensed discharge from two Leyden jars is employed.

CORRESPONDENCE.

INDUSTRIAL HOLIDAYS.

To the Editor of the *Chemical News*.

SIR,—I enclose a copy of a letter which has been sent to all Trades Unions, Employers Associations, and the members of both Houses of Parliament, Lord Mayors, and Mayors.

Those who are interested in the question will be very glad if you can see your way to give it publicity in your columns.

SIR,—The incidence of public holidays, though hallowed by custom, is uneconomic and inconvenient both to manufacturers and workpeople.

It is now suggested that the Whitsuntide holiday should be dispensed with, and that in its place a full week's holiday during the summer or autumn months should be substituted.

If this suggestion were adopted, it might be found desirable to divide the country up into trade areas—say, twelve in number—and to arrange for the areas to take their holidays in successive weeks.

The advantage of this plan—from the point of view of those who cater for holiday makers—would be obvious, as it would give them a steady trade spread over a quarter of the year, instead of a glut of business at intervals.

I should be very grateful if you would be so kind as to let me have your opinions and criticisms of this proposal as soon as possible.—I am, &c.,

PERCY CREED.

MISCELLANEOUS.

The Swedish Royal Academy of Science.—Sir William Crookes, O.M., F.R.S., has been elected an Honorary Foreign Member of this Academy.

Monosodium Tri-ferri-sulphate.—This salt, $3\text{Fe}_2\text{O}_3 \cdot \text{Na}_2\text{O} \cdot 4\text{SO}_3$, may, like its congener, the potassium salt, be prepared from solutions of aluminium sulphate containing iron by precipitation with sodium carbonate, and represents an exsiccated sodium alum:—

Salt taken	0.185 gm.
H_2O	0.123 "
BaSO_4	0.015 "
$\text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$	0.050 "

The above analysis of the salt obtained in this way represents the sodium present regarded as present in an amount comparable with the errors of experiment, and the water, regarded as water of crystallisation, $2\frac{1}{2}\text{H}_2\text{O}$; the alumina and ferric oxide being isomorphically interchangeable. The SO_4 estimation alone in this experiment would give the formula of the salt as required. A further experiment for the amount of Fe_2O_3 gave the Fe_2O_3 calculable to the above salt as Fe_2O_3 , also within the error of experiment, as giving the formula of a salt, $5\text{Fe}_2\text{O}_3 \cdot \text{Na}_2\text{O} \cdot 4\text{SO}_3$, possible.—J. C. THOMLINSON, B.Sc.

MEETINGS FOR THE WEEK.

TUESDAY, 27th.—Royal Institution, 3. "Geological War Problems," by Prof. J. W. Gregory.

— Royal Society of Arts, 4.30. "Land Settlement in South Australia," by Hon. F. W. Young.

THURSDAY, 22nd.—Royal Institution, 3. "Modern Improvements in Telegraphy and Telephony—Telephony," by Prof. J. A. Fleming.

FRIDAY, 30th.—Royal Institution, 5.30. "Recent Developments of Molecular Physics," by Prof. J. H. Jeans.

SATURDAY, 31st.—Royal Institution, 3. "Russian Idealism—The Ideas of the Russian Philosopher, Vladimir Solovoyof," by Stephen Graham.

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THE CHEMICAL NEWS

VOL. CXV., No. 2992.

THE TRAINING OF THE CHEMICAL STUDENT FOR WORK IN THE FACTORY.*

By F. G. DONNAN, F.R.S.

I HAVE already dealt with this most important subject in previous publications (*Journal of the Society of Chemical Industry*; *The Chemical Trade Journal and Chemical Engineer*; *Engineering Supplement of The Times*, July 28, 1916). To these I must refer for a fuller consideration of the subject than is perhaps possible here, and confine myself to the question of the training of the chemist in engineering science. In this connection there appear to me to be three possibilities; that is to say, three broad divisions as regards the training of a man who is going in after-life to be concerned in some fashion or in some degree with the carrying out of chemical processes on a factory scale.

1. We may give a man a thorough and extensive chemical training, but combine with it a certain amount of training in engineering principles and methods.

2. We may give a man a pretty extensive training in both chemistry and engineering.

3. We may induce men who have received or are receiving a thorough training in engineering to devote some time to a further study of chemistry, and to turn their attention to the design and working of chemical plant and apparatus.

I am well aware that it is not usually possible in actual life and practice to draw hard-and-fast distinctions and to schedule in any system of precise categories the knowledge and experience of particular men. Nevertheless, in a discussion of this sort one must adopt some such system, and so for the sake of clearness of thought I propose to classify as follows:—

CLASS 1. *Chemists* (Research Chemists).

CLASS 2. *Engineer-Chemists*.

CLASS 3. *Chemical Engineers*.

Hitherto our general practice in Great Britain and Ireland (with certain notable exceptions, however) has been to keep the chemist and the engineer apart, both in training and in after-life. In my opinion this practice has resulted in enormous damage to the progress and efficiency of our chemical and allied industries. We find the engineer with little or no knowledge of, or training in, chemistry in charge of the design, erection, and control of chemical plant and processes. We find him acting as process-manager and as general works manager. Nor can we blame him. Somebody has got to build the mill and make the wheels go round. We find the chemist on the other hand too often figuring as a humble "tester" (so-called "analyst") and general hanger-on to the coat-tails of the engineer-manager. This state of affairs, which all chemists must deplore, is, however, very frequently a necessary consequence of the narrow training and restricted outlook of the chemist. It is not a question merely of working in glass flasks or in metal pans. The real reason is that his training has been too narrow and specialised. He can calculate the results of an analysis. But he cannot calculate anything else. He lacks all engineering sense. He has no idea of the mechanics, the hydrostatics, the hydraulics, the thermophysics, the thermochemistry, and the thermodynamics of chemical processes. He cannot even apply the physics he has

learnt. He cannot calculate heat transfer, heat efficiency. He has not been trained to think in terms of energy-efficiency at all. Nowadays he has usually learnt a little physical chemistry. But he has no idea of the vast field of application of physical chemistry in chemical industry. And as for the determination of quantitative bulk-time flow-sheets, and the calculation of the costs of power, labour, repair, depreciation, &c., he has never been given a chance to think in such terms. Yet everything I have mentioned most intimately concerns him, if he is to take his rightful place in the development and control of our chemical and allied industries.

Let me give my idea of the successful development of a new process in a well-organised industrial corporation. Let us suppose that the chemists of the research department have worked out a new process in the laboratory. They will combine in intimate co-operation with men of classes (2) and (3) in designing and testing a quite small trial plant. During this process the *special chemical engineering data* will be obtained. All three will then combine to work out the design, control, and overhead and running costs of a technical unit plant. If this appears favourable—and here the financial man has a large say in the matter—the plant is erected. In this operation the work of the engineer is very important. But it must be the chemists and the engineer-chemists who control the testing and running of the plant, who find out its imperfections, and continually strive to remove them and so improve the economy and efficiency of the process. The working of the whole plant must be subjected to rigid scrutiny and precise calculation in every detail. The thermophysics, the thermochemistry, and the thermodynamics—mention only three great essentials—must be fully worked out and understood. The engineer-chemists, and especially the chemical engineers, must see to it that the most economical and the most labour-saving machinery is employed, whilst the research chemist (or "chemist" as I have called him above), before he returns to his laboratory to work out fresh problems, must organise an accurate and detailed system of chemical and physical testing and control.

Needless to say, in actual life such sharp lines of demarcation in the division of work will not always exist. The research chemist may become an engineer-chemist or *vice versa*, or either may develop a special faculty for chemical engineering. There must be plenty of latitude allowed for the exercise and development of natural aptitudes and special abilities.

Let us now turn our attention to the training of the three classes of men dealt with above.

Men of class (1) are of course absolutely necessary. They are the discoverers of new compounds and new reactions and of the precise conditions of velocity and equilibrium. Their special field will in general be the research department. But if they are to exercise their proper vitalising and fertilising action in the organism, they must be highly-educated men of wide outlook and horizon. They cannot bring their special powers into fullest action if they are confined to the laboratory. They must therefore be able to co-operate intelligently with classes (2) and (3). In order to do this, one essential is that they should possess a good knowledge of *physics* and *physical chemistry*. And undoubtedly they will require some idea of engineering science. Just how much it is very difficult to say. But a course of applied mechanics and engineering drawing is certainly necessary. And I would add to that some practical thermochemistry and thermodynamics as exemplified in the drawing up of energy balance sheets for various energy-transformers, e.g., boilers, furnaces, gas producers, steam-engines, gas-engines, economisers, heat-exchangers, &c. Such studies will implant in their minds the ideas of calculation and efficiency which are so lacking in the usual chemical training. Men of class (2) are required in great numbers—indeed, in far greater numbers than men of class (1). They should receive a very considerable amount of engi-

* A Contribution to a General Discussion on "The Training and Work of the Chemical Engineer," held by the Faraday Society, March 6, 1917.

engineering training, but it must be somewhat specialised for their proper sphere of work. Besides the matters already mentioned, they should possess a good knowledge of—

(a) Physical and chemical properties of materials of construction (wood, metals, alloys, refractories, glazes, enamels).

(b) Methods of testing materials of construction; strength of materials.

(c) Motion of liquids and gases; hydraulics; valves, pumps, &c.

(d) Thermophysics, including heat transfer.

(e) *Principles of design* and working of all the chief known types of chemical plant and machinery, and a good knowledge of the chief chemical technological processes.

(f) Generation and transmission of power; fuel economy.

(g) Construction of flow-sheets, calculation of costs, and design and lay-out of factories.

(h) The use of engineering tools.

In addition to such things, it is needless to remark that men of this class must possess certain essential qualities of *temperament*—sound “horse” sense, cool quick judgment, power of controlling workmen, courage in the face of danger. Without these qualities of character and temperament no knowledge will be of any use. Concerning men of class (3), the essential thing is that they are thoroughly trained engineers. The more chemistry they know, the better it will be. But here again it is difficult to say how much. This much one can, however, say, and say with certainty—in chemical engineering there lies the greatest and the most lucrative field of development for engineering science. I do not think that many British engineers are alive to this fact, though it is one of vital importance.

To our standard schools and institutions of civil, mechanical, electrical, heating, illuminating, and aeronautical engineers, we must add without delay schools and institutions of chemical engineering.

Other nations are already far ahead of us in this respect. There is not a moment of time to be lost. I wish now to say a few words concerning the time and method of training of the chemists and engineer-chemists. As regards the former, the culmination of their training must consist generally in the carrying out of one or two chemical researches in the chemical laboratories of the universities and higher technical schools. Their business is to be expert investigators of scientific problems. The intellectual equipment for this business is the same, whether these men remain in the universities or enter industrial research departments. A minimum of five years' training is required for this. But I would advise the directors of industrial corporations, when looking for men of high capacity, to consider the body of young university lecturers. Provided reasonably good salaries and prospects can be offered, our industrial directors who understand their business will find a rich field here awaiting encouragement and development.

The culmination of the training of the engineer-chemist must certainly also be “research.” But it is research of a different, though equally important, sort. It is the investigation of the precise conditions which determine how a given chemical process can best be carried out on a technical scale. There is no better way of doing this than by directing the attention of the student to some substance, reaction, or patented process which appears to possess, or which may, if developed, possess, commercial interest and importance. The research then consists in the investigation of the precise quantitative optimum conditions of the reaction, the determination of the various physical and engineering data required for the design of plant to carry it out, and the actual construction and running of a small experimental plant wherein the process is realised. It is just here that the greatest lacuna in our present educational institutions exists. We want and *must have*

cheap rough buildings—sheds, if you like—well supplied with water, power, steam, gas, draught, and drainage, where such things can be done. They must be supplied with foundries, forges, and engineering shops where the necessary gear can be made with reasonable facility. And, indeed, the young engineer-chemist will learn a good many lessons of practical life in these shops. It is also my hope that many young well-trained engineers, the “chemical engineers” of the future, will make use of such “laboratories” also, and will, as part of their training, co-operate with the young engineer-chemists in the economical and scientific realisation of chemical processes. I do not think that such “operation laboratories” need be terribly expensive, as some people fear. The real essential is that the work should be everywhere accurate and quantitative as regards materials, energy, and cost. I regard the work of the engineer-chemist as essentially *applied physical chemistry*. If we interpret that expression correctly and with sufficient width of view, I think we shall find therein the key to the whole situation. The engineer-chemist is a chemist, not an engineer. But he must be a chemist with a wide knowledge of physical chemistry and imbued with the *spirit* and method of the best type of engineer.

I estimate the minimum time for his period of training at five years. During this period of time he will gain much if he can work during some of his long vacations in chemical or allied factories. I make a solemn appeal to our manufacturers to arrange this. I appeal to them also to provide money for the carrying out of the things I have indicated above. We can do nothing if they will not help us. We must speed up our intellectual potential. There is not an hour to be lost. Otherwise the declaration of peace will be but the reopening of our previous condition of senile decay—a pleasant reward, indeed, for the hosts of young men who have risked their health and life on our behalf. Let us not ask for State protection until we can *prove* that we deserve it and are fit to derive national benefit therefrom. To him that hath shall be given.

THE ATOMIC VOLUMES OF OXYGEN AND THE HALOGENS AT THE CRITICAL POINT.

By GERVAISE LE BAS.

ONLY a comparatively few substances have been studied at this point.

CARBON AND HYDROGEN.

The relation $C=4H$ has been shown to exist in the normal paraffins and in the ring compounds benzene and hexamethylene. The absolute volume of this unit is, however, different in the two classes of compounds.

H 9.67 in the normal paraffins.
8.52 in ring compounds.

(See the *CHEMICAL NEWS*, 1908, xcviij., 85).

OXYGEN.

The free volume of oxygen is—

O : O_{Vm} 53°0 (2×26.5) (Cailletet and Matthias).

It has been shown that, at the boiling-point, the position of oxygen in the hydrocarbon chain has some influence upon the volume of oxygen.

Terminal oxygen.	Symmetrically placed oxygen.
7.2	10.8

The same thing is observed at the critical point.

$C_2H_5 \cdot O \cdot H$	$C_2H_5 \cdot O \cdot C_2H_5$
V_m 216.6	281.3
22×9.8	29×9.7
215.6	281.3

It follows that the volume of—

Terminal oxygen		Symmetrically placed oxygen
O'		$>\text{O}$
is 2×9.8	and	3×9.7
19.6		29.1
Mean value, 21.2 .		

This is very similar to one of the values attributed to oxygen. At any rate it is interesting to find that the atomic volume of free oxygen is intermediate between those of alcoholic and ethereal oxygen, practically the mean.

The volume of carbon dioxide is—

CO_2	V_m	..	98.0
	C	..	38.8
O_2	..	..	$59.2 (2 \times 29.6)$

It follows that $>\text{O} = 29.6$, which is the same as that of ethereal oxygen. This is equivalent to 3×9.8 , and thus the volumes of these two classes of oxygen, under the conditions, are equal to three times the unit. The relative volumes are—

H	O'	$>\text{O}$	O''
1	2	3	3
Acetic acid, $\text{CH}_3\text{CO}_2\text{H}$.		Methyl ester, $\text{H.CO}_2\text{CH}_3$.	
170.5		171.1	
171.0		18×9.5	171.0

Since acetic acid is to some extent associated at the critical point, association as such exerts but little or no effect on the volume.

THE ESTERS.

(From van 't Hoff's text book "Lectures on Theoretical or Physical Chemistry").

	V_m	Δ	
HCOOCH_3	171	57	$3 \times 57 = 171$
$\text{H.COOC}_2\text{H}_5$	228	57	$4 \times 57 = 228$
$\text{CH}_3 \text{COOC}_2\text{H}_5$	285	57	$5 \times 57 = 285$
$\text{CH}_3 \text{COOC}_3\text{H}_7$	343	58	$6 \times 57 = 342$
$\text{H.COOC}_5\text{H}_{11}$	401	58	$7 \times 57 = 399$
			$W 18$
			$W 24$
			$W 30$
			$W 36$
			$W 42$

The volumes of the isomeric esters are nearly the same as those given above.

Since $V(\text{CH}_2)$ is $57 = 6 \times 9.5$, $V(\text{O}_2) = 57$ in the acids and esters. This shows that, under the conditions, O_2 occupies the same volume as CH_2 . It follows that $\text{O}' = 3\text{H}$, $>\text{O} = 3\text{H}$. The volume of O_2 in combination, 57 , is very similar to its volume in the free state, 53 . It is concluded that, at the critical point, oxygen possesses a relative volume of 3, except alcoholic oxygen, which occupies 2 unit volumes or stereo. And so other conditions—boiling, melting-points, solid state—oxygen tends to assume its normal volume, 2H .

THE HALOGENS.

	V_m	R.	Δ	
Fluorine, F—				(F)
$\text{C}_6\text{H}_5\text{F}$	$270.4 (Y)$	247.8	22.6	22.6
Chlorine, Cl—				(Cl)
$\text{C}_6\text{H}_5\text{Cl}$	$306.5 (Y)$	247.8	58.7	58.7
CCl_4	$276.2 (Y)$	38.8	237.4	4×59.3
CH_3CHCl_2	236.0	116.4	119.6	2×59.8
Bromine, Br—				
$\text{C}_6\text{H}_5\text{Br}$	$322.4 (Y)$	247.8	74.6	
Iodine, I—				
$\text{C}_6\text{H}_5\text{I}$	$348.4 (Y)$	247.8	100.6	

The relative volumes of the halogen atoms at the critical point in terms of combined hydrogen, ($\text{H } 9.7$), are—

F.	Cl.	Br.	I.
22.6	58.7	74.6	100.6
2.3	6.0	7.7	10.4

The volumes of these atoms at the boiling-points are—

F.	Cl.	Br.	I.
8.5	21.7	27.0	37.0
2.4	6.0	7.5	10.3

($\text{H} = 3.6$).

There is thus the usual 8.3 ratio between the volumes of these atoms at the boiling and critical points.

RESEARCHES ON QUINAZOLINES.*

A NEW AND SENSITIVE INDICATOR FOR ACIDIMETRY AND ALKALIMETRY, AND FOR THE DETERMINATION OF HYDROGEN-ION CONCENTRATIONS BETWEEN THE LIMITS OF 6 AND 8 ON THE SORENSEN SCALE.

By MARSTON TAYLOR BOGERT and GEORGE SCATCHARD.

(Concluded from p. 141).

Experimental.

Dinitrobenzoylene Urea, $\text{C}_8\text{H}_4\text{O}_6\text{N}_4$.—20 grms. anthranilic acid were dissolved in 700 cc. water and 15 cc. concentrated hydrochloric acid (calculated, 12 cc.) by warming. The solution was filtered, cooled, a solution of 15 grms. KNCO (calculated, 12 grms.) in 50 cc. water added slowly with mechanical stirring, this stirring being continued for twenty minutes after all the KNCO solution had been added. The uraminobenzic acid precipitated as a pasty white mass of microscopic needles. 300 grms. NaOH were added with cooling. This dissolved the uramino acid, and the sodium salt of benzoylene urea soon separated in crystalline form. After standing for four hours the sodium salt was filtered out, dissolved in a litre of boiling water, precipitated with acetic acid, the free benzoylene urea filtered out, washed with water, and dried at 120° . Yield, 21.8 grms., or 92 per cent. The product formed colourless needles, m. $353-4^\circ$ (corr.), which m. could not be raised by further crystallisation.

Ten grms. of this benzoylene urea were heated on the water bath with 100 cc. concentrated sulphuric acid (which did not quite dissolve it all), and 12 cc. (calculated, 8 cc.) concentrated nitric acid (grms., 1.42) added. Heat was evolved, and the mixture turned bright red, but soon changed to bright yellow. After heating for an hour at 100° the mixture was cooled and poured into a litre of ice and water, the precipitate filtered out, washed with water, and recrystallised from a litre of 50 per cent acetic acid. The crystals were removed, washed, and dried at 120° . Yield, 14.4 grms., or 92 per cent.

Subs., 0.2026, 0.2786; H_2O , 0.0290, 0.0419; CO_2 , 0.2846, 0.3895.

Calculated for $\text{C}_8\text{H}_4\text{O}_6\text{N}_4$ —C, 38.08; H, 1.60. Found—C, 38.31, 38.13; H, 1.60, 1.68.

Subs., 0.1858, 0.1655; 36.60 cc. N at 17° and 765.4 mm.; 32.75 cc. N at 20° and 795.3 mm.

Calculated for $\text{C}_8\text{H}_4\text{O}_6\text{N}_4$ —N, 22.19. Found—N, 22.28, 22.30.

As thus prepared the compound formed pale greenish yellow prisms, decomposing at $274-5^\circ$ (corr.), which decomposition point could not be altered by further recrystallisation.

100 cc. of its aqueous solution saturated at 23° gave 0.0164 grm. residue at 110° , and 100 cc. of the water gave

* From the Journal of the American Chemical Society, xxxviii, No. 8.

0.0007 grm. residue. This solubility of 0.0157 grm. per 100 cc. is equivalent to 0.00062 mols. per litre, and corresponds to 14–15 drops of 0.01 molar indicator solution to 10 cc. of liquid to be tested.

The substance is very difficultly soluble in cold alcohol, or in ether, benzene, toluene, ligroin, chloroform, carbon tetrachloride, or carbon disulphide; slightly soluble in acetone, ethyl acetate, cold acetic acid, or boiling alcohol; moderately soluble in boiling water; readily soluble in boiling glacial acetic acid. It can be recrystallised from water or acetic acid. In solution of sodium hydroxide or carbonate it dissolves with a yellow colour, but is reprecipitated from such solutions by saturation with CO_2 .

For the preparation of the sodium salt 25 grms. of the dinitrobenzoylene urea were dissolved in 115 cc. molar NaOH and 500 cc. boiling water, the solution filtered and cooled. A mass of long bright yellow needles crystallised out. These were removed, pressed as dry as possible, and then left over concentrated sulphuric acid in an evacuated desiccator. The rest of the dinitrobenzoylene urea was recovered by acidifying the filtrate. The sodium salt thus dried *in vacuo* was then heated to constant weight at $140-150^\circ$.

0.3195 grm. subs. lost 0.0194 grm. H_2O . Calculated for $\text{C}_8\text{H}_3\text{O}_6\text{N}_4\text{Na}\cdot\text{H}_2\text{O} - \text{H}_2\text{O}$, 6.17. Found— H_2O , 6.07.

Subs. (dried at $140-150^\circ$), 0.3001; NaSO_4 , 0.0777. Calculated for $\text{C}_8\text{H}_3\text{O}_6\text{N}_4\text{Na}-\text{Na}$, 8.39. Found— Na , 8.38.

The solubility of the salt at 20° and at 2° was determined by taking a measured volume saturated at the desired temperature, heated to boiling, acidifying with hydrochloric acid, cooling, filtering out the precipitated dinitrobenzoylene urea, and drying to constant weight at 120° in a Gooch crucible. This gives the difference in solubility between the sodium salt and the free dinitrobenzoylene urea.

1. 50 cc. solution saturated at 20° gave 0.4898 grm. dinitrobenzoylene urea, indicating a solubility of 0.0389 mols. per litre, or 1.1359 grms. $\text{C}_8\text{H}_3\text{O}_6\text{N}_4\text{Na}\cdot\text{H}_2\text{O}$ per 100 cc.
2. 50 cc. solution saturated at 2° gave 0.1294 grm. dinitrobenzoylene urea, indicating a solubility for the sodium salt of 0.0103 mols. per litre, or 0.3008 grm. per 100 cc.

In both the above calculations the solubility of free dinitrobenzoylene urea at the temperature used has been assumed as zero. This of course is not strictly accurate, as the free dinitrobenzoylene urea is itself slightly soluble; but it is sufficient for all practical purposes, and those who wish closer figures can readily obtain them from the solubility results recorded above for the free dinitrobenzoylene urea.

The indicator solution was prepared by dissolving 0.292 grm. of the salt in 100 cc. water, and was therefore 0.01 molar. The dropper used delivered 22–23 drops per cc. Fifteen drops of this indicator solution in 10 cc. 0.01 molar HCl gave no precipitate; 20 drops gave considerable. The solubility is thus about four times the amount ordinarily used in practice.

Determination of Hydrogen-ion Concentration.—Phosphate and borate solutions were prepared as described by Sørensen. To 10 cc. of each four drops of indicator solution were added. That with an index of 6 gave a colourless solution, while that with an index of 8 gave a distinct greenish yellow, the colour developing evenly in the intermediate solutions.

Borate solutions with an index of 9 and 10 gave the same colour as those with 8; 11 gave a slightly deeper colour. 0.1 molar NaOH (index 13) gave a much deeper greenish yellow, one drop of the indicator giving as much colour as four drops in a solution with index of 8.

Effect of Toluene and of Chloroform.—Phosphate solutions were prepared of index 6.4, 7.0, and 7.6. 30 cc. of

each solution were made up, and each of these solutions then divided into three lots of 10 cc. each. These separate lots were then grouped into three sets of three lots each, one of each index. One set was shaken with excess of toluene and filtered. Another set was given a similar treatment with chloroform. The third set was kept as a blank. Four drops of indicator were then added to each solution. No difference could be detected between the solutions of the same concentration in the three sets.

Effect of Protein.—25 cc. of egg white were diluted to 100 cc. with water, filtered, and 2 cc. of this solution added to a mixture of 14 cc. primary and 6 cc. secondary phosphate solution. This was then divided into two 10 cc. portions, to one of which β -nitrophenol was added, and to the other the new indicator. Both showed an index of 6.60.

Salt Effect.—160 cc. secondary phosphate solution and 40 cc. primary phosphate solution were mixed, and 12 grms. NaCl (approximately molar) added. Electro-motive force measurements of this solution showed an index of 6.74, while the new indicator gave 6.90. Such a solution is more concentrated than any generally measured. The effect is apparently due to the large concentration of Na^+ ion, which is responsible for the presence of unionised salt molecules which are coloured like the ion.

Fading Effect.—Three sets each were made up of phosphate solutions of index 6.6 and of 7.6. Four drops of indicator were added to one set upon a certain day, to the second set on the second day, and to the third set on the third day. On this third day no difference could be detected between the three sets of the same concentration. After standing for a week the first set was compared with freshly prepared standards with the following results:—That with index of 7.6 had faded to 7.45–7.50, and that with index of 6.6 to 6.55–6.60.

Titrations.—Titrations of 0.01 molar NaOH and HCl , using 10 drops indicator, gave 1.00011, 1.0004, 1.0009, and 1.0006 for the ratio of base to acid.

Titrations of 0.1 molar NH_4OH and HCl , using 10 drops indicator, gave 1.1257, 1.1262, and 1.1261 for the ratio of acid to base.

Titrations of 0.1 molar acetic acid and NaOH , using 5 drops of indicator, gave 1.0129 and 1.0138 for the ratio of base to acid, but it was necessary to titrate by comparison with a colour standard instead of to the first appearance of a yellow colour.

Effect of Temperature on the End-point.—Two 100 cc. samples of 0.005 molar NaCl (the approximate concentration at end-point of titrations of 0.01 molar solutions) were heated to boiling, and 10 drops of indicator added. One was titrated to one side of the end point and the other to the other side. On cooling, no change was observed in the colour in either case.

Effect of Nitrous Acid.—30 cc. molar HCl were diluted to 200 cc. (making it 0.15 molar), 1.5 grms. NaNO_2 (0.1 molar) added, and 40 drops of indicator (10 drops per 50 cc.). After standing for an hour at room temperature the solution was heated to 65° for a few minutes, cooled, and then titrated twice with 0.1 molar NaOH . A sharp end-point was obtained in both cases, and the results checked closely, viz., 1.0716 and 1.0715.

Summary.

A dinitrobenzoylene urea has been discovered whose mono-sodium salt is a very sensitive indicator for hydrogen-ion concentrations between the limits of 6 and 8 on the Sørensen scale, changing from colourless to greenish yellow.

Structurally, and in its behaviour as an indicator, it resembles β -nitrophenol more closely than any of the other well-known indicators. Like the latter, its chief disadvantage is its yellow colour, which renders it unsuitable for work in artificial light.

It is but slightly affected by neutral salts, not at all by chloroform or toluene, proteins (egg albumen) have no

more influence upon it than upon *p*-nitrophenol; its colour fades very slightly in a week, and is unchanged by nitrous acid. It can be used in cold or in boiling (100°) solutions. It gives a sharp end-point with NH_4OH and HCl , but cannot be used to titrate carbonates.

For the preparation of neutral ammonium citrate solutions, for fertiliser or soil analysis, it should prove superior to rosolic acid (commercial carnalline).

It can be prepared easily from anthranilic acid by the method described.

The experimental work upon which this paper is based was carried out by Mr. George Scatchard in partial fulfilment of the requirements for the degree of Doctor of Philosophy under the Faculty of Pure Science of Columbia University.

Acknowledgments are also due to Dr. H. A. Fales, of this University, for much valuable assistance and advice.

DENSITY OF RADIO-LEAD FROM PURE NORWEGIAN CLEVEITE.

By T. W. RICHARDS and C. WADSWORTH.

THROUGH the kindness of Prof. Eilen Gleditsch of the University of Kristiania, we have been so fortunate as to receive a specimen of lead sulphide from carefully selected Norwegian cleveite. According to Dr. Gleditsch, "The Norwegian uraninites are very old and very unaltered. They are found in well developed crystals and occur in connection with the pegmatite dykes in south-eastern Norway." The sample in question occurred in cubic crystals near Langesund.

As Hönigschmid has already pointed out (*Sitz. Wien. Akad.*, 1914, lxxiii., II.a, 20), the properties of radio-lead obtained from pure minerals of this sort are far more interesting and significant than those of lead obtained from ordinary uranium ores, which doubtless contain some admixture of ordinary lead. (The name radio lead is used provisionally to designate lead which appears to be the result of radioactive transformation). Hönigschmid has shown that the lead from pure cleveite has an atomic weight as low as 206.06, and our own experience with the sample referred to above essentially confirms this result, as will be shown in another communication. So far as we know, however, the density of lead of this kind has not yet been determined, and accordingly the present paper recounts such a determination, which forms an interesting sequel to the recently published results on the density of Australian radio lead (*Journ. Am. Chem. Soc.*, 1916, xxxviii., 221).

The purification of the sulphide, which doubtless contained traces of sulphides of other metals, was carried out as follows:—The specimen was dissolved in nitric acid and crystallised three times with centrifuging as nitrate,—a process which Baxter's experience has shown to be an excellent one for the purification of lead from other metals. (Baxter and Grover, *Journ. Am. Chem. Soc.*, 1915, xxxvii., 5). From this purified nitrate the chloride was precipitated by pure hydrochloric acid, and this salt was crystallised three times. The final crystals, after draining on the centrifuge, were stored in a vacuum desiccator over caustic soda. The chloride thus prepared was used for the determination of the atomic weight, the density being determined in the material saved from the filtrates from that determination. These filtrates contained excess of silver, therefore enough hydrochloric acid was added to bring the concentration of the dissolved chloride ion to 0.01 normal, because at this concentration silver chloride is most nearly insoluble (G. S. Forbes, *Journ. Am. Chem. Soc.*, 1911, xxxiii., 1937). When the precipitated silver chloride had settled and had been removed by filtration through a Gooch-Munroe crucible with platinum mat, the resulting solution was concentrated and crystallised once more as nitrate. The pure crystals were electrolysed,

and the pure radio-lead treated exactly as in the case of the other samples previously described (*loc. cit.*, p. 224).

The amount of substance at hand being rather small, the work could not be done quite as accurately as before. The density determinations were made in the same pycnometer as before, by the second method described on p. 223 (*loc. cit.*)—the volume of the pycnometer having been redetermined because its tip had been broken in the meantime. Four identical determinations gave 5.7200 as the weight of water in the pycnometer at 19.94°, weighed in air. Therefore, the volume of the pycnometer was 5.7361 cc.

Density of Lead from Cleveite.

Obs. wt.	Wt. in vac (W).	Obs. wt. water not displaced.	Corres. volume.	Volume of pyc.	Volume of water displaced.	Density W/V.
4.4252	4.4250	5.3287	5.3427	5.7361	0.3924	11.277
4.4252	4.4250	5.3286	5.3436	5.7361	0.3925	11.274
4.4252	4.4250	5.3285	5.3435	5.7361	0.3926	11.271
4.4252	4.4250	5.3285	5.3435	5.7361	0.3926	11.271

Average, 11.273

The density of this sample, presumably a nearly pure isotope, is thus 11.273, distinctly less than 11.289, the density of the Australian radio-lead, and still less than the density 11.337 found for ordinary lead. The decrease is almost exactly proportional to the decrease of the atomic weight in these samples, for the atomic weight of the Australian lead was about 206.35, and that of this sample 206.085. Thus the atomic volume of the isotope—

$$(206.08)/(11.273) = 18.281,$$

is almost identical with that of pure lead, as indicated by our previous experiments. 18.281 is essentially equal, within the limit of error of experiment, to the value 18.277, found for ordinary lead, and to the value 18.279, found for Australian radio-lead. It is interesting to note that Australian radio-lead would be essentially duplicated as to these properties by a mixture consisting of three parts of pure isotope to one of ordinary lead.

Summary.

This brief paper describes the determination of the density of lead from Norwegian cleveite kindly furnished by Prof. Gleditsch. This lead, presumably a pure isotope, was found to have a density (11.273) decidedly lower than the mixture previously studied. The corresponding atomic volume of the pure isotope is essentially equal to that of ordinary lead, as indicated by the earlier results on radio-lead from Australia.—*Journal of the American Chemical Society*, xxxviii., No. 9.

DETERMINATION OF FLUORINE IN SOLUBLE FLUORIDES.

By J. G. DINWIDDIE.

IN determining fluorine gravimetrically there are several methods in use. The method of Rose (*Liebig's Ann.*, 1849, lxxii., 343) consists in precipitating calcium carbonate together with calcium fluoride so that the precipitate of calcium fluoride may, with some degree of satisfaction, be filtered and washed. After being ignited the calcium carbonate is dissolved out by means of 1.5 N acetic acid, and the residue of calcium fluoride is washed, ignited, and weighed. This procedure is open to two objections, that the calcium fluoride is very appreciably soluble in the dilute acetic acid, and that two filtration are required. Starck and Thorin (*Zeit. Anal. Chem.*, 1912, li.) precipitate calcium fluoride along with a known weight of calcium oxalate and determine the fluorine by difference. These authors claim that the precipitate so formed is

granular and easy to wash, but Adolph found it very hard to handle (*Journ. Am. Chem. Soc.*, 1915, xxxvii., 2500). Starck makes use of the mixed chloride and fluoride of lead (*Zeit. Anorg. Chem.*, 1911, lxx., 173). This method is said to give good results provided that care is taken to use very little wash-water.

In the attempt to precipitate fluorine so that it could be separated from fluosilicic acid by filtration, an excess of powdered calcium sulphate, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, was used. This gave a precipitate of calcium fluoride and sulphate which was easier to filter and wash and had almost no tendency to run through the pores of the filter. It was thought that it might be possible to adapt this to the determination of fluorine in soluble fluorides. Calcium fluoride when treated with sulphuric acid is converted to sulphate, the fluorine being expelled as hydrofluoric acid. Now, if a mixture of fluoride and sulphate of calcium be similarly treated with sulphuric acid, the only change will be the conversion of the fluoride to sulphate. A gram molecule of calcium fluoride, 78, when changed to sulphate will weigh, 136, so that an increase of 58 parts by weight will mean that the precipitate contained 78 parts of calcium fluoride.

In perfecting this method there were several difficulties which arose in connection with the filtering, ignition, &c., of the precipitates. These will be enumerated, and then will be described the expedients which were used to avoid these difficulties.

1. Since the fluoride has to be treated with acid, it cannot be filtered on asbestos because the hydrofluoric acid set free will attack the mineral of the filter.

2. If an ordinary filter is used particles of the precipitate adhere to it, and, when burnt along with the paper, the calcium sulphate is partly turned to sulphide and leads to incorrect results.

3. If the mixed precipitate is heated to redness in order to obtain a constant weight the mass fuses together, and it is almost impossible to completely decompose the solid mass with sulphuric acid so as to convert all of the fluoride to sulphate.

4. When the excess of sulphuric acid is being driven off so that the residue of calcium sulphate may be weighed, great care has to be exercised to prevent spattering if the heat is supplied by placing a Bunsen burner beneath the crucible.

The detailed directions for the determination of fluorine by the use of powdered calcium sulphate as mentioned above will now be given, and it will be made clear how each of the above difficulties was surmounted.

The solution of the fluoride, which should occupy as small a volume as practicable, say, about 30 or 40 cc., and should be neutral, is heated to boiling, and powdered calcium sulphate is added. After standing for thirty minutes to one hour, with frequent stirring, the precipitate of fluoride and sulphate of calcium is washed by decantation several times, and then put into the filter for final washing. The filter consists of a perforated platinum crucible in the bottom of which is a small disc of ashless filter-paper, cut so as to fit exactly in the bottom without being bent up around the sides. By keeping gentle suction upon the crucible the disc is held in place, and the filtrate comes through without the least turbidity. As soon as the precipitate has been sufficiently washed it is transferred with the aid of a fine jet of water from a wash-bottle to an ordinary platinum crucible; the disc of paper is washed free of the precipitate, and is ignited on the lid of the crucible, while the precipitate in the crucible is evaporated on the steam bath to dryness. If now this residue is heated to redness to obtain a constant weight it melts, and becomes very difficult to decompose with sulphuric acid. By experimenting it was found that at a temperature around 300°C . the calcium sulphate loses all of its crystal water, and a constant weight is obtained. The proper temperature is obtained by heating the platinum crucible within an ordinary iron crucible of diameter about 3 inches at the top, used as a radiator. In order to equalise the heat a thin piece of asbestos was placed in the bottom,

and upon this was placed a small triangle for the platinum crucible to rest upon. By heating the bottom of the iron crucible with a Bunsen burner to a low red the contents of the platinum crucible reach a constant weight within one hour or less.

When a constant weight has thus been obtained the residue is mixed with a little water and several cc. of pure sulphuric acid. This mixture is now evaporated on the steam-bath as far as it will go at this temperature, and then, by heating further, the sulphuric acid is driven off, the last traces requiring the application of a red heat for a few moments. As was stated above there is great danger of spattering when the excess of acid is being driven off. In order to avert this danger and to permit the acid to be driven off very quickly the following method was adopted:—The lid is placed on the crucible, which is resting on a triangle. A Meeker burner is fastened above, and slightly to one side of the crucible by means of an adjustable clamp. The flame of the burner is allowed to impinge from above at an angle of about 45° on the farther side of the lid of the crucible. In this way the heat can easily be regulated so that the sulphuric acid volatilises rapidly, and since the heat radiates from above there is almost no tendency to spatter. The residue obtained by igniting at 300° consists of a mixture of calcium fluoride and sulphate, while the residue remaining after volatilisation of the sulphuric acid consists entirely of calcium sulphate. The increase in weight of the contents of the crucible is due to the replacement of two atoms of fluorine by the sulphuric acid radical. The changes which have taken place may be represented by—



Thus, 84 of sodium fluoride gives 78.0 of calcium fluoride and 136.07 of calcium sulphate. Therefore 58.07 of increase corresponds to 84 of sodium fluoride and 78 of calcium fluoride, and to estimate the calcium fluoride present in the precipitate multiply the increase in weight by $78/58.07 = 1.3431$, and for the sodium fluoride multiply by $84/58.07 = 1.4465$.

In order to test out the method which has been described in detail a solution of pure sodium fluoride was used. Commercial sodium fluoride, even that marked C.P., contains silica, and so, for a standard solution, pure hydrofluoric acid was neutralised to phenolphthalein with pure sodium hydroxide obtained by allowing moist air to act on metallic sodium in absence of carbon dioxide. This solution was diluted so that it contained about 3 grms. of sodium fluoride per 100 cc. To ascertain the exact concentration of this solution, first the method of Rose, of precipitating the fluoride along with the carbonate of calcium, was tried. This precipitate was so hard to handle in that it ran through into the filtrate, and clogged up the pores of the paper as well, that the attempt was abandoned. Since the solution of which the standard was desired contained no other compound besides sodium fluoride, its concentration was finally determined by evaporating measured portions to dryness in a platinum crucible, igniting to about 300°C ., and weighing. The following results were obtained on several portions:—Ten cc. portions of the sodium fluoride solution gave 0.2724, 0.2721, 0.2723, 0.2725, 0.2721 grm. of sodium fluoride. One determination with 20 cc. gave 0.5450 grm. The average of all gave for the standard of the solution that 10 cc. contained 0.2724 grm. of sodium fluoride.

Table VI. shows the results obtained by carrying out the determinations as outlined above.

On account of the solubility of calcium fluoride there will be a tendency for the results to run low, and, unless the filtrate and washings are kept to a low volume, large negative errors are liable to occur. In several determinations the filtrate was about 200 cc., and the results here were about 1.4 per cent low. On account of this danger a solution saturated with pure calcium fluoride and calcium sulphate was used for wash-water in order to eliminate the solubility error, and results very close to the calculated

value were obtained even when the filtrate was allowed to get quite large. These results are shown in *h* and *i* of Table VI.

TABLE VI.

	Sol. NaF used. Cc.	NaF	Increase F ₂ → SO ₄	NaF equiv.	Diff.	Error. Per cent.
a.	10	0.2724	0.1894	0.2740	+0.0016	+0.62
b.	10	0.2724	0.1888	0.2731	+0.0007	+0.25
c.	10	0.2724	0.1885	0.2727	+0.0003	+0.11
d.	10	0.2724	0.1882	0.2723	-0.00017	-0.062
e.	10	0.2724	0.1883	0.27237	-0.00003	-0.015
f.	10	0.2724	0.1876	0.2714	-0.0010	-0.37
g.	20	0.5448	0.3752	0.5427	-0.0021	-0.385
h.	10	0.2724	0.1881	0.2721	-0.0003	-0.082
i.	10	0.2724	0.1886	0.2728	+0.0004	+0.11

The weighed precipitate of calcium fluoride and sulphate might be converted, according to Loczke (*Zeit. Anal. Chem.*, 1910, xlix., 329), into chloride and sulphate by evaporating with hydrochloric acid, and the calcium sulphate be weighed, the fluoride being determined by difference. However, this would require another filtration and would be less accurate.

Since, during the precipitation of the fluoride of calcium by the sulphate, an equivalent amount of sulphate ion is set free, it is obvious that this method is adopted without any modifications to the separation and determination of fluorides in the presence of sulphates. It may also be used for the separation of fluorine from other radicals which do not form insoluble compounds with calcium.

The method of Bunsen for determining fluoride in the presence of phosphoric acid would be applicable here provided that it were accurate. This consists in weighing a mixed precipitate of orthophosphate and fluoride of calcium, and then converting it to phosphate and sulphate by ignition with sulphuric acid. He claims that the final residue after ignition consists entirely of calcium orthophosphate and calcium sulphate, but Treadwell and Koch (*Zeit. Anal. Chem.*, xlii., 469), in experimenting to decide upon the best method for this separation in wines and beers, heated a weighed amount of calcium orthophosphate with sulphuric acid, as directed by Bunsen, until a constant weight was obtained. Instead of obtaining the original weight they obtained a much greater weight. Upon testing the residue they found that the precipitate contained a large amount of calcium sulphate, and that metaphosphoric acid had been formed and condensed partly on the lid of the crucible. *American Journal of Science*, xlii., p. 464.

THE EFFICIENCY OF CALCIUM CHLORIDE, SODIUM HYDROXIDE, AND POTASSIUM HYDROXIDE AS DRYING AGENTS.

By GREGORY P. BAXTER
and
HOWARD W. STARKWEATHER.

In a recent paper upon the efficiency of certain drying agents, Baxter and Warren (*Journ. Am. Chem. Soc.*, 1911, xxxiii., 340) make the statement that Dibbitts (*Zeit. Anal. Chem.*, 1876, xv., 159) found the aqueous vapour pressures of the lowest hydrate of calcium chloride to be 0.29 mm., 2.17 mm., and 3.50 mm. at 0°, 24°, and 30° respectively. Our attention has been called by Dr. W. F. Hillebrand to the fact that these figures refer to a hydrate containing 26 per cent of water. As we have been unable to discover reliable data upon the drying efficiency of anhydrous calcium chloride, the matter has been investigated experimentally (see, however, Marden and Elliott, *Journ. Ind. and Eng. Chem.*, 1915, vii., 320). We have found the efficiency of this salt to be far greater than the above values indicate. In addition, we seized the opportunity

to test two other common drying agents, fused sodium and potassium hydroxides.

The air current method was employed, the details of the apparatus and procedure being essentially identical with those described by Baxter and Warren. Calcium chloride was prepared in an anhydrous condition by fusion in an open platinum dish. (The calcium chloride was undoubtedly basic after fusion; it is, however, unlikely that the basic impurity was present in quantity sufficient to affect the results even if of a greater efficiency than the neutral salt). While still warm it was crushed to pieces the size of a small pea and packed in a glass-stoppered U-tube about 15 mm. in diameter, the column of salt being about 30 cm. long. (In the paper by Baxter and Warren it is erroneously stated that the column of salt was 30 mm. long, as in reality it was ten times this length). In most of the experiments the air was passed over a 20 per cent solution of sodium hydroxide to ensure an excess of moisture before being conducted through the calcium chloride tube. After a considerable amount of moisture had been absorbed by the calcium chloride, in a few experiments the air was first dried by means of concentrated sulphuric acid in order that the equilibrium might be approached from the reverse side. The results with calcium chloride at 0° and 25° were very consistent and satisfactory, but the first experiments at 50° showed gradually higher values for succeeding experiments. Fearing that the chloride had by this time absorbed so much water that its efficiency had been impaired, the salt was again fused. While the results then became more nearly concordant, irregularities still persisted, until the layer of active salt was doubled to about 70 cm. by inserting a second U-tube containing the fused salt. The results then showed the most satisfactory agreement. In order to find out whether the layer of chloride had been sufficiently long at the lower temperatures, additional experiments—Nos. 4, 5, 13, 14—were carried out at the lower temperatures with the longer layer, with results identical with the earlier ones (see Table I.).

The attempt was made to weigh the phosphorus pentoxide tube in which the water was absorbed to hundredths of a mgrm., by using a No. 10 Trömmner balance and gold plated weights carefully standardised by the Richards method. No claim is made, however, that the accuracy is greater than a tenth of a mgrm. It was repeatedly shown that the tube remained constant in weight within this amount for periods of fourteen to sixteen hours.

No blank experiments were considered necessary, since in the runs with potassium hydroxide the gain in weight of the tube was scarcely perceptible.

While three points are obviously insufficient to define a curve exactly, since the plot of the logarithm of the vapour pressure against the reciprocal of the absolute temperature is very nearly a straight line it seems worth while to point out that the preceding averages can be represented by the modification of the Antoine formula (*Comptes Rendus*, 1890, cx., 632; 1891, cxii., 284; 1892, cxiii., 328; 1893, cxvi., 170)—

$$\log v. p. = 8.614 - \frac{3234}{T + 58}$$

The desiccating efficiency of sodium hydroxide was determined in the same manner as that of calcium chloride, using the two tubes (70 cm.) of drying agent. The sodium hydroxide was fused in a silver dish and broken up while still warm. Apparently the greater part of the water was absorbed by the first 5 cm. of the hydroxide (see Table II.).

The experimental values may be computed from the expression—

$$\log v. p. = -4.041 \frac{373.3}{(T - 414)}$$

Potassium hydroxide was next investigated in the same way. The potassium hydroxide was fused in a silver dish, and while still warm was broken into small pieces and transferred to the drying tubes. Two experiments at 25°

and two more at 50°, each involving nearly twelve litres of air, gave changes in the weight of the phosphorus pentoxide tube no greater than the error of weighing. Then two experiments at 50°, each extending over three days, were performed. Air was actually passing through the apparatus only during the day; at night all stopcocks were closed (see Table III.).

TABLE I.—CaCl₂ as Drying Agent.

No. of expt.	Conditions of experiment.	Litres per hour	Litres of air (0° 760 mm.).	Mgms. of water.	Cc. of water vapour (0° 760 mm.).	Internal pressure of system, mm.	Pressure of water vapour, mm.
Temperature, 0°.							
1.	Moist	1.1	5.8	0.41	0.51	770	0.07
2.	"	1.0	5.8	0.45	0.56	763	0.07
3.	"	1.2	5.8	0.50	0.62	764	0.08
4.	"	2.3	5.7	0.50	0.62	750	0.08
5.	Dry	1.5	5.8	0.40	0.50	761	0.07
Average							0.07
Temperature, 25°.							
6.	Moist	1.3	6.38	1.85	2.30	758	0.27
7.	"	0.8	5.71	1.93	2.40	761	0.32
8.	"	0.8	5.82	2.43	3.02	768	0.40
9.	"	1.0	5.73	2.15	2.67	761	0.35
10.	"	1.2	5.84	1.97	2.45	770	0.32
11.	"	2.3	5.78	2.00	2.49	768	0.33
12.	"	1.0	5.66	2.40	2.99	752	0.39
13.	"	1.0	5.63	1.90	2.36	746	0.31
14.	Dry	2.0	5.67	2.01	2.50	750	0.33
Average							0.34
Temperature, 50°.							
15.	Dry	1.2	5.72	8.18	10.17	758	1.35
16.	Moist	2.3	5.66	7.96	9.90	752	1.32
17.	Dry	1.3	5.76	7.80	9.70	765	1.28
18.	Moist	1.3	5.63	8.17	10.16	749	1.35
19.	Dry	2.9	5.69	8.60	10.70	751	1.41
20.	Moist	0.9	5.50	8.08	10.05	738	1.33
Average							1.34

TABLE II.—NaOH as Drying Agent.

Temperature, 0°.							
1.	Moist	2.0	11.6	0.60	0.75	765	0.05
2.	Dry	2.0	11.4	0.35	0.44	755	0.03
3.	Moist	1.6	11.3	0.40	0.50	745	0.03
Average							0.04
Temperature, 25°.							
4.	Moist	2.0	11.43	2.00	2.49	756	0.16
5.	"	1.1	5.69	0.90	1.12	752	0.15
6.	Dry	2.0	11.43	1.82	2.26	756	0.15
Average							0.15
Temperature, 50°.							
7.	Moist	1.4	5.69	6.82	8.48	756	1.13
8.	Dry	1.7	11.42	14.07	17.50	761	1.16
9.	Moist	1.7	11.55	13.90	17.30	763	1.15
Average							1.15

TABLE III.—KOH as Drying Agent.

Temperature, 50°.							
1.	Moist	2.0	39.9	0.28	0.35	759	0.007
2.	"	2.3	45.6	0.34	0.42	759	0.007
Average							0.007

As pointed out by Morley (*Am. Journ. Sci.*, 1885, xxx., 441), there is a possibility in these long experiments that water diffused through the rubber connections, or was formed by oxidation of the rubber. (Only one very short rubber connection was used in our apparatus before the air reached the phosphorus pentoxide tube). In view of this possibility the results are to be considered as maxima. No weighable amount of moisture could have passed the pentoxide, since Morley found that phosphorus pentoxide leaves not more than 1 mgrm. of water in 40,000 litres of air (*Am. Journ. Sci.*, 1887, xxxiv., 199; *Journ. Am. Chem. Soc.*, 1904, xxvi., 1171).

The noteworthy facts shown by the foregoing results are—(1) The very considerable temperature coefficients in the case of calcium chloride and sodium hydroxide (Baxter and Warren found similar increments with rising temperature with the salts examined); and (2) the remarkable efficiency of potassium hydroxide even at 50°. Judging from the temperature coefficients of the other two salts, potassium hydroxide at 25° is fully as efficient as sulphuric acid.

To summarise the results of this research, the aqueous vapour pressures of the lowest hydrates of the salts examined have the following maximum values:—

	0° (mm.).	25° (mm.).	50° (mm.).
CaCl ₂	0.07	0.34	1.34
NaOH	0.04	0.15	1.15
KOH	—	—	0.007

The weights of residual water in 1 litre of a gas dried at 25° by these compounds, calcium bromide, zinc chloride, zinc bromide, and sulphuric acid, are—

Substance.	Mgms.
CaCl ₂	0.36
CaBr ₂	0.2
ZnBr ₂	1.1
ZnCl ₂	0.8
NaOH	0.16
KOH (50°)	0.007
KOH (a)	0.002
H ₂ SO ₄	0.003

(a) Estimated from the temperature coefficient of the other salts.

—*Journal of the American Chemical Society*, xxxviii., No. 10.

THE ELECTRO-ANALYSIS OF SILVER WITH SOLUTIONS OF SILVER CHLORIDE IN AMMONIA.

By E. P. SCHOCH and F. M. CRAWFORD.

A METHOD for the quantitative electro-deposition of silver out of solutions of silver chloride in ammonia has not been published so far, but the use of this electrolyte appears to be very desirable, because it is likely to yield pure deposits while the cyanide electrolyte—the only other solvent for silver chloride heretofore employed in electro-analysis—produces impure deposits.

We have found that approximately 99.6 per cent of the silver in an ammoniacal solution of silver chloride can be deposited by electrolysis in good form. It is merely necessary to increase the conductivity of the solution by adding enough of an ammonium salt (ammonium chloride) to the solution, and to electrolyse with a small current density at the ordinary temperature.

In order to deposit the small remnant of silver left in the electrolyte, the ammonia is neutralised with a slight excess of hydrochloric acid, and a weak reducing agent (oxalic acid) is added; from this electrolyte the remainder of the silver may be deposited completely and in good form. The presence of nitrates (or of nitric acid in the original mixture) does not affect the result.

Care must be taken to clean the platinum cathode thoroughly, to keep the current density small in order to avoid "burning" the deposit, and to wash and handle the electrode with the deposit *gently*, to avoid knocking off the deposit. With a little care on these points, the determination is easily carried out and gives satisfactory results, as is shown below.

The following determinations were made with the electrolytic apparatus described in a paper by Schoch and Brown (*Journ. Am. Chem. Soc.*, xxxviii., 1660):—Samples of pure sheet silver were dissolved in concentrated nitric acid and the silver was precipitated with a slight excess of hydrochloric acid. With several of the samples, the silver chloride was filtered, washed, and dissolved in a slight excess of concentrated ammonia; and with others the original mixture (containing the excess of nitric acid) was treated with ammonia. About 20 grms. of ammonium chloride and enough water were added to each mixture to bring the volume to approximately 150 cc. (enough to cover the electrodes), and the solutions were electrolysed at room temperature with an initial ampère of 0.35 amp. (which with our apparatus required 1.2 volts between the electrodes). This voltage was kept constant until the current had dropped to zero; care had to be taken to reduce the current promptly while the metal was being deposited, because the maximum allowable current density (which cannot be exceeded without obtaining a dark and loosely adherent deposit) rapidly becomes less as the silver content of the solution becomes less. When the ampère had become practically zero, the voltage was allowed to rise gradually to 1.3 to 1.4 volts and electrolysis continued until a total of twenty-five to thirty minutes had elapsed. This period must necessarily be larger if the quantity of silver to be deposited is greater than that which we used.

Deposition of Silver.

Silver present. Grm.	Found. Grm.	Error. Grm.	Error. Percent.
0.1595	0.1591	-0.0004	-0.25
0.5887	0.5886	-0.0001	-0.02
0.3704	0.3699	-0.0005	-0.14
0.2958	0.2956	-0.0002	-0.07
0.4030	0.4027	-0.0003	-0.07
0.5139	0.5139	—	—
0.2551	0.2551	—	—

Then, without disturbing the apparatus, about 3 grms. of oxalic acid crystals were added to the solution, and enough concentrated hydrochloric acid to make the solution faintly acid to litmus paper. Without increasing the applied voltage, electrolysis was continued for about twenty minutes. Then the experiment was terminated, and the electrodes were washed and dried in the manner described by Schoch and Brown (*loc. cit.*). The results obtained are given in the accompanying table.—*Journal of the American Chemical Society*, xxxviii., No. 9.

Friedel and Craft's Reaction.—Eyvind Bødtker and O. M. Halse.—The inverse Friedel and Craft's reaction generally occurs, though not always with the same facility. The xylenes cannot be split at all, while a hydrocarbon, such as cymene, containing two different alkyls is very readily decomposed. It is known that aluminium chloride, or the metal alone, can be used as a catalyst in the preparation of chloro- or bromo-benzene. If care is not taken to use only small quantities of the catalyst the bromine and iodine compounds are transformed into the β -diiodo halogen compounds, while chlorobenzene resists the action of aluminium chloride. When dichloro- or dibromobenzene is boiled with an excess of benzene and a little aluminium chloride it is found that the reaction $2C_6H_5Br = C_6H_4Br_2 + C_6H_6$ is not reversible.—*Bull. Soc. Chim. de France*, xix.-xx., No. 12.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, March 15, 1917.

Sir J. J. THOMSON, O.M., President, in the Chair.

PAPERS were read as follows:—

"Initial Wave Resistance of a Moving Surface Pressure." By Prof. T. H. HAVELock, F.R.S.

Hitherto the wave-resistance associated with the motion of an assigned pressure system over the surface of water has been studied only in the steady state for uniform motion. The present work is an attempt to calculate this quantity at any time for a system which has been suddenly established and set in uniform motion at a certain instant. The method is applied first to a waveless system for which the integrals can be evaluated exactly. A comparison is made between the exact solution and that obtained by Kelvin's group method of evaluating similar integrals. Approximate solutions are then obtained in certain cases when the pressure system leaves a train of regular waves in its rear. The various results are analysed graphically and numerically so as to obtain some estimate of the time required before the steady state is practically attained.

"Experiments with Mercury Jets. I. The Relation between the Jet length and the Velocity of Efflux. II. A Comparison with Jets of other Liquids." By Prof. S. W. J. SMITH, F.R.S., and H. MOSS.

It has probably been noticed by those who have worked with mercury "dropping electrodes"—in which the mercury issues in a narrow stream from the drawn-out end of a vertical tube—that the length of the jet alters in a peculiar way with the length of the mercury column producing it. The results of a study of this phenomenon are given.

The first part of the paper describes, and attempts to define exactly, how the jet-length, for different velocities of efflux, alters with the diameter of the jet and with the surface tension between the mercury and the solution into which it falls. An interpretation of the results is given.

The second part of the paper continues the study by comparing the behaviour of mercury jets in air with that of other liquids and connects the present observations with the well-known experiments of Savart.

In each part the attempt to correlate the phenomena is based mainly upon Lord Rayleigh's theory of jets, and it is found that the experiments provide confirmations of this theory which are wanting in those of Savart. In addition, the observations throw some light upon the nature of the initial disturbance which determines the jet-length and suggest further experiments that might be undertaken.

"Mode of Approach to Zero of the Coefficients of a Fourier Series." By Prof. W. H. YOUNG, F.R.S.

"Dissipation of Energy in the Tides in Connection with the Acceleration of the Moon's Mean Motion." By R. O. STREET.

On the hypothesis of non-turbulent motion harmonic with respect to the time with period twelve hours, an expression is obtained for the mean rate of dissipation of energy by viscosity in a portion of the ocean in the form of a surface integral over that area of a function of the surface current-velocities only.

This integral has been evaluated over the greater part of the Irish Sea, the mean rate of dissipation obtained being 5×10^9 foot poundals per second. In the absence of external forces, this rate of dissipation would cause the energy to be reduced in the ratio e to 1 in about two hours. If the rate of dissipation per unit area for the whole ocean were the same as in the Irish Sea, the total frictional loss of energy by the tides would be at the mean rate 6×10^{13} foot poundals per second.

If the apparent lunar acceleration is attributed to a slowing of the earth's axial rotation, a retardation of the order four minutes of arc per century per century is necessary for its explanation. This retardation implies a decay of the earth's kinetic energy of rotation at the rate 1.6×10^{13} foot poundals per second, which is about a quarter the mean rate of dissipation of tidal energy on the above hypothesis. A maximum surface current velocity of two feet per second over the whole ocean would give rise to sufficient dissipation to account for this retardation of the earth.

SOCIETY OF GLASS TECHNOLOGY.

Ordinary Meeting, March 15, 1917.

Mr. S. N. JENKINSON, in the Chair.

The following papers were read:—

"Some Remarks about the Development of Glass Furnaces on the Continent." By T. TEISEN.

The methods of heating furnaces were first considered. Wood and even peat were used in Scandinavia in some works, whilst natural gas was used in the United States to some extent. The chief fuel in use for furnaces, however, was coal, either burned direct or converted into gas. When coal is burned direct a large excess of heat is necessary to complete the combustion, and if this large excess be cut down the waste gases contain a large proportion of carbon monoxide. In the complete combustion of 1 kilogram of coal to carbon dioxide, 8000 calories are set free, whilst only 2500 calories are freed if the coal only burned to carbon monoxide. Thus the presence of carbon monoxide in the waste gases represents a considerable loss of heat.

The use of producer gas allows much better combustion to be obtained, so that a large excess of air is unnecessary. A higher temperature results therefore, particularly if the gas and also the incoming air are delivered hot to the combustion chamber. This preheating of air and gas can be accomplished in two ways—(1) by regeneration; (2) by recuperation.

In the latest pattern of the Siemens regenerative furnace there are four chambers with fire-bricks, two of which are being heated by the waste gas, whilst the other two are warming up the incoming air and gas. By reversing the direction of flow of air and gas, the chambers which were being heated now supply heat to the air and gas, whilst the others are in their turn heated by the waste gases. This method of regeneration is very useful for large furnaces, but is expensive and takes up considerable floor space.

In the Hermanssen system of recuperation the air and gas always pass in the same direction and are sufficiently preheated by passing through flues which are surrounded by the hot waste gases. In 1906/7, the first Hermanssen furnace used for glass-melting was burning wood, and melted a batch of 4 cwt. in ten hours. So perfect a combustion is got in the Hermanssen furnace that at the Costa Works, crystal glass is made in open pots. Furnaces of this type will melt glass during the night for next day, and so the capacity of a furnace should not be judged by the number of pots, but by the amount of glass it will melt. From this point of view the continuous recuperative furnace is more efficient than the regenerative furnace.

Considerable discussion ensued, the points raised bearing chiefly upon the relative advantages of the two systems of regeneration and recuperation, and the applicability of each system to tank as well as pot furnaces.

"The Effect of small amounts of Impurities, in particular Chlorides and Sulphates, in producing Turbidity or Opacity in Glass." By W. E. S. TURNER and J. D. CAUWOOD.

The work originated in troubles that had been experienced by manufacturers using Russian potash as one of

the components of a lead batch. The glass made with Russian potash though found at first to be quite clear gradually became milky as it stood at a lower temperature in the pot, or if after the glass had been worked the articles in course of formation were reheated. Analysis indicated that the three impurities in Russian potash to any extent were phosphate, chloride, and sulphate. Of these three, phosphate was not active in producing milkiness, at least up to 1 per cent. of the batch mixture, but chloride and sulphate did cause opacity. Of the two, sulphate was the more powerful, and even potassium sulphate to the extent of $\frac{1}{2}$ per cent of the batch produced opacity, when melting at 1300° was carried out until the glass was clear, followed by several hours' heating at $950-1000^\circ$. Under the same conditions to give opacity, chloride must be present to an extent exceeding $\frac{1}{2}$ per cent of the batch.

It was possible to prevent or retard the appearance of milkiness by the addition of borax. The most effective agent, however, is high temperature, by which chloride is volatilised or sulphate decomposed. The results emphasised the need of the introduction of more efficient furnaces, capable of reaching a high temperature. Especially was this so when dealing with the new types of glassware that now had to be produced in this country.

In the discussion that followed, it was pointed out that whilst borax removed the milkiness, on the glass being reheated it again appeared. Thus, the best means of removing this defect was to employ a high temperature.

Prior to the above meeting, members of the Society were conducted round the works of the Icknield Glass Company, and the visit was much appreciated.

The next meeting of the Society will be held in the University, Sheffield, on Wednesday, April 18, at 2 p.m.

SOCIETY OF CHEMICAL INDUSTRY.

(LONDON SECTION).

Ordinary Meeting, March 5, 1917.

Mr. ARTHUR R. LING in the Chair.

The following paper was read and discussed:—

"Composition of Power Gases." By W. A. TOOKEY, M.I. Mech. Eng.

The author called attention to the fact that the development of the gas engine since its early days has been entirely independent of the varying composition of power gases, while the proper method of using them has been mainly the result of experiments in the testing shops at manufacturers' works. He referred to the scientific research work that had been carried out in connection with the working fluid of internal combustion engines, but stated his opinion that this work was somewhat of a negative character as far as the gas engine maker was concerned, and the progress in gas engine work had not been greatly assisted by science.

Reference was made to an extended series of tests which the author had carried out for the two chief London gas companies since 1911, and to the necessity that arose in connection with those tests of instituting a basis of comparison other than the usual statements with regard to consumption of gas per cubic foot to indicated horse-power developed. In this way it had been found far preferable to compare the outputs of widely varying engines in respect of mean pressure developed behind the piston per unit of mixture strength, and it was shown that upon this basis the performance of internal combustion engines, whether working with liquid or gaseous fuels of all the various kinds in use, were wonderfully similar, and, indeed, practically identical when account was taken of the clearance volume ratios of the engines concerned.

A chart was exhibited showing output consumption curves of eight very dissimilar engines in support of this

fact, and from this the author deduced that as far as the composition of gas was concerned, it mattered little to the internal combustion engineer. What was of more concern to him was the calorific value of the strength of mixture; that is to say, of the gas, air, and residuals which took part in the combustion at each impulse.

The author proceeded to point out that having regard to mixture strength basis in proportion to mean pressure developed on the system he enunciated, it was clear that the progress of the last thirty years could be explained, namely, that in general terms the reduction in the rate of gas consumption has been coincident with the decrease of clearance volume in relation to total cylinder volume which mechanical improvements have permitted and as time brought about new methods of ignition.

The author stated that in his practice he endeavoured, first of all, to obtain such mixture strength as his experience had found to be practically universal for full load outputs whatever the size or type of engine. By properly correlating the ignition-point and noting the shape of the indicator diagram then secured, one could almost tell what the consumption of gas was without the use of any gas measuring device, so uniform seemed to be the operation of the engines in respect of gas consumption.

The author then proceeded to discuss the effect upon variations in calorific value, pressure, &c., upon the engine, keeping the supply of air constant. He gave charts showing the recorded variations in composition and calorific value of suction gas at full load and no load, and also exhibited a chart showing that however wide the variation of calorific value in various power gases ranging from natural gas to blast-furnace gas, yet when these had been mixed with the theoretically correct proportion of air to provide complete combustion, there was very little difference between them, or rather that the range of variation in quality was greatly limited, more so than would at first sight appear to be possible.

The author then dealt with the next question of pre-ignition, and discussed whether the hydrogen percentage in gas composition was actually so troublesome as it was commonly supposed to be. He gave practical examples of pre-ignition troubles which rather tended to show that the proportion of hydrogen content has very little to do with it, and that it was more likely that pre-ignition troubles of the nature alluded to was consequent upon a change from a slow burning mixture to one which was fierce to burn.

In conclusion, the author stated that as far as his experience went he thought that, speaking generally, the actual composition of power gases was not of great importance, and certainly of much less importance than the cleanliness, uniformity of pressure, and invariable composition.

DISCUSSION.

Mr. G. N. HUNTLY said that he was first inclined to think that the author was introducing a variable factor in taking break horse-power instead of indicated horse-power as a co-ordinate in his calculations, but from the diagram shown he had quite justified this course. He regarded the statement that over a wide range the efficiency of the gas engine was independent of the calorific value of the fuel, since gas was bought in cubic feet and not in B.T.U., there was a possibility of misconception.

Mr. W. J. A. BUTTERFIELD was of opinion that engineers had not given sufficient attention to the minor constituents of the gas, such as, for instance, carbon-bisulphide, the temperature of ignition of which was very low. Pre-ignition might possibly be due to its presence. Acetylene was a gas of high calorific power and low temperature ignition, and insufficient attention, he thought, had been given to its behaviour in the gas engine in comparison with the other gases and oils.

Mr. P. H. JOSELIN said that having had considerable experience in stripping gas and never having seen the calorific power reduced by more than 7 per cent, although 5 per cent was about the average, he could not understand

why the consumption in a gas engine should increase 10 to 15 per cent, as quoted by Mr. Tookey, when running on stripped gas.

Prof. J. S. S. BRAME said that he agreed with the author that hydrogen probably had no determining effect on pre-ignition, and that the cause must be sought, as far as the charge was concerned in the minor gaseous constituents, probably acetylene. Mr. Butterfield's suggestion of carbon bisulphide being a possible cause of pre-ignition was worth following up. Referring to the author's remarks on the variability in composition of suction gas, he said that what the curves really showed was that with the engine running at a steady output, the calorific value of the gas was uniform. It was only when changes of load occurred that great variation in the gas was noted, the composition of the gas adapting itself to load conditions.

Mr. J. HINCHLEY asked whether there was any conclusion to be drawn from the fact that one of the engines, a Norwegian, was the most efficient. He also suggested to the author that his remarks, without further interpretation, might lead one to suppose that no real improvement had been made in gas engines for thirty years.

Dr. R. LESSING asked whether the remarkable uniformity of curves obtained from a variety of fuels was not due to the fact that the amount of combustible matter in the mixtures was comparatively small, and the calorific value of the mixtures per cubic foot of cylinder space was made uniform by the different air requirements of each fuel. A rich fuel, such as town gas, had to be diluted down to practically the same calorific strength as a mixture made by producing a poor calorific gas. However, he thought the composition of fuel gas and the constitution of their components must influence the working of an engine.

Mr. W. McLAREN, speaking as an engineer, advocated better companionship between the chemist and the engineer. He said that very frequently when things went wrong it was the engineer who got the blame. They would not hear so much about producer gas if the gas companies had given them better terms in the past.

The CHAIRMAN said that he must join with the members in thanking Mr. Tookey for his paper. With regard to pre-ignition, he had been struck by Mr. Butterfield's remarks as to the importance of the minor constituents, and more especially carbon bisulphide, which was an endothermic compound and under certain conditions was explosive.

Dr. R. SELIGMAN asked if it was to be understood that gas of low calorific power could be used in the gas engine as well as Mond gas.

The AUTHOR, in reply, stated that the density of the gas was of no practical importance. Rich coal gas of density 0.4 could be switched off to suction gas of density 0.8. The timing of ignition needed variation in town gas as compared with producer gas—the latter requiring the ignition point to be set slightly earlier. With stripped gas reduced by 5 per cent in calorific power, the ignition was irregular and involved 13 per cent increased consumption. As soon as the mixture was strengthened, however, by admitting more gas the ignitions became more regular and the increased consumption fell to 5 per cent. He did not want it to be thought that he was condemning suction gas. Installations of this type of gas making plant were doing good work all over the world, being used with such variable fuels as cotton-seed, charcoal, waste wood, and almost all combustible material, but the plant needed adjustment if highest efficiency was to be maintained under all conditions of everyday operation.

The next Ordinary Meeting of the London Section will be held at the Chemical Society's Rooms, Burlington House, Piccadilly, on Monday, April 2, 1917, at 8 p.m. The following papers will be read:—

"Further Notes on the Action of Acetic Acid on Aluminium." By RICHARD SELIGMAN, Ph.D., and P. WILLIAMS. In continuation of their studies, the present paper describes experiments on the action of acetic acid

generally on aluminium at different concentrations and temperatures. The authors have examined the effect of the addition of a number of salts which may be present in commercial acetic acid, and in this connection have obtained some striking results. At the same time they have elucidated the conditions which determine whether the attack of acetic acid is local or general.

"Nitrated Castor Oil." By R. BRIGHTMAN. The author has studied various means of producing nitrated castor oil, and finds that the nitration is best conducted by means of dilute nitric acid. He has determined the composition of the product and various constants, and concludes that it is a triglyceride of the nitric esters of ricinoleic acid.

The Annual Meeting of the Liverpool Section will be held on Wednesday, April 4, in the Muspratt Lecture Theatre, Chemical Laboratories, at the University, at 6 p.m.

After the business is concluded, Prof. R. ROBINSON will read a paper on "The Industry of the Catechol Derivatives."

NOTICES OF BOOKS.

Chemical Discovery and Invention in the Twentieth Century. By Sir WILLIAM A. TILDEN, F.R.S., D.Sc., LL.D., Sc.D. London: George Routledge and Sons, Ltd. New York: E. P. Dutton and Co. Pp. xvi + 487. Price 7s. 6d. net.

THE author of this book is to be heartily congratulated upon having done a real service to science in preparing a highly interesting account of recent work in chemistry. There is hardly any more difficult task than to write a popular scientific work, and the difficulties have possibly never been so successfully met as in this case. The needs of the student and of the general reader who is interested in the development of the science are equally considered, and the author has shown particular skill in providing just the information which lies beyond that obtained by the student in his regular work. Excellent accounts of important discoveries—of argon and radium, for example—are given, very often in the words of the original workers, and throughout the book stress is laid upon the value of the pursuit of knowledge for its own sake, by which alone true progress is made. Part I. deals with chemical laboratories and the work done in them, and contains detailed illustrated descriptions of many famous laboratories in different parts of the world. The second part gives accounts of modern discoveries and theories, such as the discovery and properties of radium, the genesis and transmutation of the elements, the microscopic and ultra-microscopic colloids. Perhaps almost more interesting is the third part, devoted to modern applications of chemistry, including the production of dyes, explosives, drugs, rubber, the fixation of atmospheric nitrogen, and many other industrial processes, while in Part IV., on "Modern Progress in Organic Chemistry," the problems of the synthesis of proteins, the origin of life, &c., are briefly discussed.

Annuaire pour l'An 1917, publié par le Bureau des Longitudes. ("Annual for the Year 1917, published by the Bureau des Longitudes"). Paris: Gauthier-Villars et Cie. Pp. vii + 661.

THIS annual publication contains the usual copious tables of astronomical data and important meteorological statistics. Physical and chemical data are not tabulated in this number, but will be given in the annual of 1918. Articles on the Babylonian Calendar, on the adoption of legal summer time, and on other subjects, are included.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Bulletin de la Société Chimique de France.
Vol. xix. xx., No. 12, 1916.

Ionisation of Sulphuric Acid and Neutral Potassium Sulphate in Aqueous Solutions of Medium Concentrations.—J. A. MUIR.—From the author's experiments, carried out some years ago, it appeared that in very dilute aqueous solutions the non-ionised sulphuric acid dissociates, when the dilution is increased, into SO_4H and H ions, and that this ionisation occurs with disengagement of heat. As a matter of fact, the direct study of the electrolysis of molecular solutions of sulphuric acid shows that if this mode of ionisation actually occurs in the case of the last traces of un-ionised acid, almost all the H_2SO_4 molecules ionise in more concentrated solutions giving SO_4 and 2H ions. In solutions of medium concentration potassium sulphate ionises to give SO_4 and 2K , and not the negative radical SO_4K and K .

MISCELLANEOUS.

Röntgen Society.—A General Meeting will be held on Tuesday, April 3, at 8.15 p.m., at the Cancer Hospital, Fulham Road, S.W. A Discussion on "The Future of the British X-ray Industry" will be opened by Mr. Geoffrey Pearce.

Reports of the Progress of Applied Chemistry.—The first volume of these Reports will shortly be published. The price of issue to Members of the Society of Chemical Industry will be 2s. 6d. and to non-members 5s. (plus 6d. postage in both cases). The issue will be a limited one, and those desiring copies should make early application to the General Secretary, Society of Chemical Industry, Broadway Chambers, Westminster, S.W.

Royal Institution.—The following are the lecture arrangements at the Royal Institution after Easter:—Prof. C. R. Beazley, two lectures on "Russian Development—(1) The Old Free Russia, (2) The Rise of Moscow"; Prof. Charles S. Sherrington, two lectures, (1) "Tetanus—its Prevention, Symptoms, and Treatment," (2) "Rhythmic Action in Muscle and in Nerve"; Prof. D'Arcy W. Thompson, two lectures, "Architectural Design in Organisms" and "The Laws of Growth and Form"; Prof. W. W. Watts, two lectures on "The Flow of Ice and of Rock—(1) The Movement of Glaciers, (2) The Flow of Rock"; Prof. H. S. Foxwell, two lectures on "Industrial Finance after the War—(1) The Character of the Industrial Struggle of To-day, (2) Its Financial Needs, How they can Best be Met"; Prof. Gilbert Murray, two lectures on "Pagan Religion at the Time of the Coming of Christianity—(1) Misleading Preconceptions (Dogma, Mythology, Statues), the Raw Material—Dea Roma, (2) Dea Roma, the Mystery Religions, Philosophy, Conclusion"; Prof. William Bateson, two lectures on "The Chromosome Theory of Heredity and the Alternatives"; Alfred Noyes, two lectures on "Modern English Poetry"; Prof. G. H. Bryan, two lectures on "Principles of Aerial Navigation"; Prof. Sir J. J. Thomson, six lectures on "The Electrical Properties of Gases." The Friday Evening Discourses will begin on April 20:—Prof. R. H. Biffen, "The Future of Wheat Growing in England"; J. Dundas Grant, "The Organs of Hearing in Relation to War"; H. Wickham Steed, "Some Guarantees of Liberty"; Prof. John Joly, "Radio-active Haloes"; Prof. Frederick Soddy, "The Complexity of the Chemical Elements"; J. Barcroft, "Breathlessness"; J. H. Balfour Browne, "The Brontës—a Hundred Years After"; Prof. Sir J. J. Thomson, "Industrial Applications of Electrons."

THE CHEMICAL NEWS

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FLUORESCENCE AND PHOSPHORESCENCE, AND THEIR USE TO PRODUCE LUMINOUS EFFECTS.*

I. THE PRODUCTION OF FLUORESCENT AND PHOSPHORESCENT EFFECTS.

By F. HARRISON GLEW.

IN general illuminants operate by incandescence, *i.e.*, the production of light through high temperature. Other processes, not involving the action of heat, are termed luminescence, and are illustrated in a few illuminants, *e.g.*, the mercury vapour lamps and, to some extent, in flame arcs.

To illuminating engineers the processes involved in luminescence have therefore a direct interest, apart from the wider aspects of these phenomena.

One of the most familiar examples of such effects is the firefly, the luminous efficiency of which is believed to be far higher than that of any existing illuminant, and other insects and marine forms of life have similar properties. The production of light appears to be due to chemical action. The glow of phosphorus (from which the term "phosphorescence" is derived) in the dark is due to slow oxidation, and luminosity may also be produced by the oxidation of pyrogallol acid and other organic materials. Such effects are termed "chemi-luminescence."

"Triboluminescence" is the term applied to luminous effects produced by friction, *e.g.*, by rubbing or scratching certain crystals (quartz, sugar, flint, &c.).

When the impact of visible light on a substance produces luminosity of a different (by Stokes's Law) a lower order) colour, this is termed "fluorescence." The effect is exhibited by flint and similar crystals. When the effect still persists after the cessation of the stimulating action so that the luminosity persists in the dark, it is termed "phosphorescence." A good example of fluorescence is to be found in the transformation of violet and ultra-violet light into visible red rays by the rhodamine reflector, used with the mercury lamp to modify its spectrum. Fluorescence may be excited by other forms of radiation, for example, that emitted by an X-ray tube, or the spark from an induction coil.

Luminous paints which, after exposure to daylight, retain luminosity for some time in the dark, have been known for many years. Crystals of calcium sulphide phosphoresce blue, zinc sulphide green; other materials give a less luminous effect in yellow, red, and other colours. The manufacture of such substances and ingredients used to accentuate their action is a complex process, as qualities quite apart from chemical purity are required. For example, the form of zinc sulphide, giving the best luminous effect on exposure to daylight, may not be that most suitable for treatment to produce continuous fluorescence.

The luminous effect induced by light in these substances is transient, diminishing greatly after a few hours in darkness. At the moment immediately after strong excitation a brightness possibly exceeding one foot-candle may be shown to exist. But in a fraction of a second this initial strong effect vanishes, and although thereafter the diminution is more gradual, a brightness below that of a white surface illuminated by moonlight is soon reached, and half an hour afterwards the luminosity is very much less

still. Experimental data on the degree of luminosity attainable by strong excitation by sources rich in ultra-violet rays are needed, but the measurements involved, as Mr. Blok will show, involve great difficulties.

Such phosphorescent substances have found various special applications. The strongest effect is produced with the substance in a powder, but, mixed with dilute varnish, it can be applied in the form of paint.

The most important practical results have so far been obtained with the self-luminous paints, which consist of zinc sulphide with a small admixture of radio-active constituents. Radium gives off three forms of rays—alpha, beta, and gamma—the former of which is responsible for the chief excitation of luminosity. Radium itself was away at a rate which will reduce it to half quantity in 1000 years. This alone, therefore, would cause an appreciable deterioration in luminous effect. In fact, however, self-luminous paints decay at a rate varying according to their radium constituent. A diminution of 50 per cent in brightness in the course of a year is not unusual, but much greater diminutions with a larger percentage of radium have been recorded. Half value in about twenty-four hours occurs with 74 mgrms. radium bromide per gm. of zinc sulphide, which strength I find to be equivalent to the light of the glowworm. On the other hand, the actual brightness, within limits, is roughly proportional to the radium content. It is therefore of very great importance to determine the order of brightness necessary for certain purposes, and not to exceed this required value, since any addition beyond this point adds to the expense and diminishes the life of the material. Up to the present time no satisfactory means of regenerating these materials has been found, although this is possible with some substances. The diminution in brightness, as stated above, cannot be attributed to decay of the radium component, and is believed to be due mainly to deterioration of the zinc sulphide during bombardment. In cases in which the powder is enclosed in glass, the transparency of this may also be affected by the radium in course of time, and the same applies to the varnish used as a binding material when the compound is applied in the form of luminous paint.

It is to be noted that the mixture with varnish is equivalent to dilution of the radium element; speaking generally, the brightness of material of given composition used as varnish will be about one-quarter of the value when used in the form of powder.

Such materials have many important applications in connection with the war, and the whole subject offers an opportunity for profitable research, and deserves to be more closely studied.

II. SOME APPLICATIONS OF FLUORESCENCE AND PHOSPHORESCENCE.

By J. S. DOW.

The subject for discussion is one on which little is generally known. These phenomena, and their relation to the complex problems underlying the production of light, are of great interest to the Society. The use of luminescence in such illuminants as the flame arc, the mercury vapour lamp, and possibly the incandescent mantle, are of interest, as suggesting the possibility of more efficient light-production than can be obtained by incandescence effects; and also because they involve free vibrations of certain wave lengths, offering the hope that eventually we may be able to control the colour of light for various purposes, as easily as we now control the intensity. The firefly has long been regarded as one of the most efficient sources of light, and researches on phosphorescent substances suggest that such forms of "cold light," though relatively feeble in intensity, have almost invariably a very high luminous efficiency. Yet the experiments on this point are a little doubtful in view of the very low luminosity, and the possibly misleading effect of the physiological complexities of the eye in such

* Introductions to a Discussion at a Meeting of the Illuminating Engineering Society, held at the Royal Society of Arts, March 22, 1917.

circumstances. From a scientific standpoint it would be very desirable to determine the luminous efficiency of such processes with greater precision.

The effect of such substances in the dark is also of interest in view of its bearing on the matter discussed at the last meeting—the influence of glare and contrast. The visibility of these substances depends very much on the state of adaptation of the eye. A small patch of luminous paint, particularly the blue light from phosphorescent calcium sulphide, can only be seen with difficulty by an eye recently adapted to ordinary artificial light. On the other hand, in the writer's experience, the brighter forms of self-luminous paint may, to a fully dark-adapted eye, produce an effect not unlike actual glare. It is therefore very important, as Mr. Glaw has suggested, to determine the minimum brightness requisite for various purposes, and not to exceed this minimum. Another effect, also clearly in evidence with the blue light of calcium sulphide, is the "spreading" of the light at distances exceeding a few feet, owing presumably to the chromatic aberration of the eye. Again, a patch subtending a small angle of the eye appears much less bright than a relatively large area, which also tends to make the surface painted fade out of sight, and, indeed, become invisible to direct vision, at a short distance away. These effects limit the applications of such substances in their more feebly luminescent forms. Except when one can deal with relatively large areas, they are best suited to near vision. For the same reasons the photometry of a small area may not give the true effect of their use over a large surface.

As regards the order of brightness met with, it would appear from tests by various observers on various self-luminous paints (zinc sulphide) that the following rough rule might be tentatively suggested, namely, that the actual brightness of freshly-prepared material in equivalent foot candles is rather less than one-tenth of the radium content in 1 gram. of composition. Thus 0.4 composition (i.e., material containing 0.4 mgrm. to 1 gram. of radium bromide and zinc sulphide), yields *about* 0.04 ft.-candles, and 0.2 composition *about* 0.02 ft.-candles (i.e., about the brightness of a white surface illuminated by full moonlight). For reasons already given, it is impossible to state such a rule with precision, but as a rough guide this may be useful. To much more powerful compositions it may not apply.

The brightness of zinc sulphide or calcium sulphide a few minutes after exposure at close range to a 50 watt electric incandescent lamp (which is typical of the type of source available to the ordinary householder) is already very much less than the "moonlight" value. From tests on some samples of the calcium sulphide "luminous buttons" now being sold for use in the dark streets, the writer has found that, after the above exposure, they were practically indistinguishable to direct vision at a distance of 10 feet, within an hour after exposure. These buttons were about $1\frac{1}{2}$ inch in diameter. The brightness in such circumstances would, therefore, not be of much help in enabling people to avoid being run over by vehicles; but they might be useful in preventing collisions of pedestrians in very dark areas. On the other hand, if such material was available in large quantities for coating kerbs, lamp posts, &c., the larger area treated would alter the problem, and they might possibly have applications in places where there is practically no artificial light provided, or in enabling a party to keep in touch with one another when traversing a wood at night. The successful use of such devices seems at present to demand conditions of such low luminosity as practically excludes the use of artificial light. Otherwise a piece of white card may appear equally bright. On the other hand, little is known regarding the persistence of luminosity excited by sources very rich in ultra-violet light, such as the quartz tube mercury vapour lamp. After such exposure effects sufficiently permanent to be used for theatrical effects are said to have been produced. Luminous paint is also said to have been used

for coating buoys and other marine objects, the luminosity induced by the sun's rays being reproduced during the dark hours of the night. In the absence of any artificial light this project seems more feasible, especially in the strong sunlight of the tropics. Luminescing materials have been found useful for many special purposes since the outbreak of war. If phosphorescing substances could be produced commercially on a large scale and at a cheap rate, new applications would doubtless present themselves (for example in underground passages and mines, for luminous danger-signs and other notices, &c., and for advertisements and spectacular purposes). In small quantities their successful use seems to demand frequent excitation by sources rich in ultra-violet rays. The writer has tried coating switches with calcium sulphide, but the relatively low general illumination in an ordinary interior is not as a rule enough to produce a useful effect.

On the other hand, the self-luminous materials, continuously excited by radium, have already many important special applications. The chief present limitations to their wider use are scarcity of supply and expense. It has, however, been recently calculated by a writer in the *Electrical World* that the weaker and less expensive forms of such materials could be used for coating switches at a cost of only 1d.— $1\frac{1}{2}$ d. per switch.

III. THE PHOTOMETRY OF LUMINESCENT SUBSTANCES.

By ARTHUR BLOK.

The measurement of the brightness of fluorescent and phosphorescent substances is rendered difficult by two factors—(i.) the colour of the light, the spectrum of which usually consists of bands or lines situated mainly in the green or blue; and (ii.) the relatively low luminosity. Both of these factors tend to introduce the Purkinje effect. Fortunately, the chief data required are usually relative, and one can thus work throughout with a coloured screen placed in front of a comparison lamp, and designed to give a colour which more or less matches the light of the material tested. If one wishes to obtain absolute values of brightness, allowance must be made for the absorption of the screen; but the procedure for affecting this introduces all the physiological difficulties attendant on heterochromatic photometry at low illuminations. An approximate colour match may be obtained fairly easily, for example, by the use of signal green glass in testing phosphorescent zinc sulphide, but unless the spectral composition of the two lights compared is substantially identical, errors may be introduced by the order of luminosity at which the test is made, the part of the retina upon which the image is received, and, perhaps, also, by the size of the photometric surface employed.

Various photometric methods have been devised for dealing with this class of substances, and in these a colour-matching screen is almost always employed. In the method described by N. E. Dorsey (*Bull. Wash. Acad. Science*, Jan. 4, 1917), a lamp is moved back and forth behind a translucent screen forming one end of a box, and the luminous compound under test is mounted on the outer surface of the screen, either in the form of paint on a card slip or in powder form in a thin-walled glass tube. Identity of colour is produced by a colour filter placed inside the box between the lamp and the screen. With this arrangement, the tested sample appears as a luminous island in a surrounding sea formed by the variably illuminated screen, and provided that a sharp line of demarcation can be obtained between the island and sea, there is much to recommend this plan—immediate contiguity of the two luminous areas under comparison greatly facilitates the determination of photometric balance.

In the method used at the National Physical Laboratory for comparing the luminosity of painted dials, a stencil replica of the dial under test is uniformly illuminated from behind by means of a glow lamp and a colour screen. The stencilled and actual dials are mounted side by side, and by means of a variable resistance the candle-power of the

lamp is brought to such a value that the luminosities of the stencilled figures and those on the actual dial are the same. By an independent calibration with a surface-brightness photometer, the brightness of the stencil for any resistance setting is known. Here, the mean effect over the whole of the surfaces viewed is judged, and as long as the dials are small there should be little difficulty in doing this. But if the dials are large, the various figures will be at different distances from the eye, and it would appear that trouble may be introduced on that account. The method, however, has the advantage that by enabling finished dials to be dealt with in their entirety it gives a final comparison of their merits, whereas if small samples of paint are measured there is always the possibility that variations in the finished article may be introduced during the painting operation, for example, by irregular mixing or uneven application of the paint.

In another scheme, developed by Prof. Clinton and Mr. Dow for measuring some very small samples in association with the speaker, the sample is viewed at a constant distance from the eye through a small opening in a white screen placed at an angle of 45° to the line of sight and to the axis of the photometer bench (the line of sight being normal to the bench axis). The opening is of such a size as to be completely filled by the luminous specimen fixed behind it—i.e., the "island and sea" plan is adopted. The inverse square of the distance of the lamp from the screen at photometric balance is proportional to the luminosity of the sample.

A point to be borne in mind in speaking of the photometric values of self-luminescent substances is that the luminosity of the material in powder form is considerably higher than when the material is mixed with varnish or other substance to form a paint. Moreover, the thickness of the layer tested to some extent determines the foot-candle value. A further factor which may influence the result in the treatment of the substance in regard to exposure to light before the test. In the case of substances like Balmain's compound, this is obviously a matter of prime importance, but with materials depending on radioactive excitants for their luminosity, the effect of previous light action is, as far as the speaker is aware, not yet thoroughly known. Indeed, it is very evident that for the systematic specification of these self-luminous substances standard test conditions still remain to be worked out.

For some purposes a single photometric measurement on any of these materials may suffice, but usually it is equally important to know the rate of luminous decay with the lapse of time. It is somewhat remarkable that although the chemical and physical sides of radio-activity and phosphorescence have been brought to a very advanced stage, very little appears to have been published on the luminous values of the substances now under discussion, and one looks almost in vain for data on the practical matter of variation of foot-candle values with time for a compound of a given nature. The present activity in night operations in war has caused a very great demand for self-luminous compounds, and, no doubt, the results of tests extending over moderately long periods will be available presently. Such tests require very great care, for at best the initial luminosities under measurement are small, and after some time they sink to values that are very difficult indeed to measure, at any rate by the eye, which after all is the instrument with which the substances are used in practice. The products now used commercially have brightnesses of the order of a few hundredths of a foot-candle, and give nearly monochromatic lights. These are conditions that tax the photometrist, and the repetition of observations to 5 or 6 per cent in tests of this nature would indicate very good work.

On the whole there seems to be a large field for the application of photometric methods in the investigation of these substances. The subject of self-luminescent materials is at the interesting stage where practical applications are emerging, and those who are conversant with the better known applications of photometry in

lighting work generally might well devote attention to the investigation of the luminous phenomena exhibited by the class of bodies now being discussed.

THE PRINCIPLE OF EXTENDED TERMS.

By F. H. LORING.

THE principle here discussed does not of course take rank with the principle of relativity or other great principles laid down by mathematicians or men of science.

Mr. H. Stanley Redgrove in the *CHEMICAL NEWS* (1915, cxii., 174) took me to task for defining *quantity of matter* as equal to or identical with *mass*. I must admit there are, so to speak, different modes of thought, but I believe more is to be accomplished by thinking in extended terms and in terms of experiment than by introducing the subtlety of logic. I will try and make this clear. For example, we start with the definition of water as (1) a combination of hydrogen and oxygen. It is then found (2) that the combination is always in a fixed proportion represented by the formula H_2O . It is further found (3) that the formula H_2O in the case of water or ice has to be increased n times: $[H_2O]_n$.

Experiment has therefore extended our terms, and it is on this ground that we may define inertia in several ways without nullifying previous statements by introducing any inconsistency, provided that the process of thought is based upon experiment. Indeed, we might write—*quantity of matter* = product of volume and density = mass or inertia = the sum of n negative electrons, and n "hydrogen electrons," &c., with the proviso that the electrical interpretation of matter, and therefore mass, must be thought of in terms of incomplete experiment.

When speaking of electrical phenomena, we may use the term *inertia*, meaning that the negative electron or electromagnetic self-induction, to take two typical examples, exhibit the properties of matter in respect of inertia; indeed, we speak of the mass of the negative electron as being $1/1700$ th that of the hydrogen atom, but we do not yet know whether the negative electron has weight and can be classed as matter. It is quite true that matter may require defining, or re-defining, in time, but in the meanwhile we need not, in my opinion, question too closely the symbols or expressions used, so long as we realise the full significance of the principle of extended terms. The final definition of matter or mass may be in terms of energy, but even then our true picture of matter will be a cinematographic mental impression of the different pictures scientists have produced by experiment.

THE QUANTITATIVE DETERMINATION OF MORPHINE IN THE VARIOUS ORGANS WHEN INJECTED INTO CATS AND RABBITS.

By A. W. HOMBERGER and J. C. MUNCH.

DURING the past few years one of the authors has had submitted to him, at different times, organs from cadavers for the analysis of poisons—especially morphine and opium. In two cases the suspects had been embalmed. In one case after seven days, and in the other after fifteen days of interment, the liver, kidneys, stomach, and spleen were brought for examination. The quantitative relations as well as the general chemical conduct of the alkaloids found in the different organs raised the question as to whether this was due to the embalming fluid, or whether the length of time after burial were the cause of the fluctuating assimilation and distribution.

The following paper deals with a series of experiments carried out on cats and rabbits in order to find, if possible,

what the effect of the embalming would be on the amount of alkaloid in the different organs in case death had resulted from alkaloid poisoning, to ascertain how much of the original product could be recovered under those conditions, and to find what organs might be the strongest assimilators of such alkaloids. The alkaloid used in this case was morphine.

The morphine used in these investigations was Merck and Company's "Morphine Sulphas," U.S.P. VIII. Qualitative examination showed it to be free from foreign materials, such as starch or other opium alkaloids. Quantitative determinations of the morphine present, by Mayer's reagent, and determinations of the sulphuric acid present, as barium sulphate, showed that the morphine sulphate used agreed with the formula $(C_{17}H_{19}NO_3)_2 \cdot H_2SO_4 \cdot 5H_2O$.

The desired amount of morphine sulphate was weighed out on an analytical balance, dissolved in distilled water, and hypodermically injected into the mesenteric circulation. After a lapse of three hours, to allow for fixation in the organs of the body, the animals were chloroformed and embalmed by cavity and arterial injection of a formaldehyde embalming fluid.

When the bodies were opened for analysis the organs were always removed in the same order, first the stomach and intestines together, then, in order, the spleen, liver, lungs, heart, kidneys, bladder, and urine, and finally the brain. Then any parts wanted for qualitative analysis were cut out. Analyses were commenced at once to avoid any changes due to further decomposition.

Autenrieth's ("Detection of Poisons," 1915, p. 57) modification of the Stas Otto process was used, with several variations, for all the quantitative extraction of the organs. A longer time of extraction, five hours (*Fourn. Am. Chem. Soc.*, 1901, xxiii., 420), three extractions with ether in both acid and sodium hydroxide solution, and Puckner's technic of final extraction by hot amyl alcohol in slightly ammoniacal solution were used. The extracted morphine was dried at 60°, and calculated to its equivalent weight of morphine sulphate. Titrations of this residue agreed, within the limits of experimental error, with the gravimetric results obtained above. Qualitative tests of all residues were made to prove that the extractions were complete.

Dragendorff's method was used for the analyses of both blood and urine (A. W. Blyth, "Poisons," 1906, p. 313). Puckner's precautions were again followed (*Fourn. Am. Chem. Soc.*, 1901, xxiii., 420). The extracted morphine was calculated to morphine sulphate, as in the Autenrieth extraction above. The weights in the following table are all expressed as morphine sulphate, $(C_{17}H_{19}NO_3)_2 \cdot H_2SO_4 \cdot 5H_2O$.

As may be noted in the table, the urine contains the largest single amount found in cats. The organs may be ranked according to morphine content, as the liver, kidneys, spleen, and stomach. The urine content shows a great fluctuation, which is explained by Magnus (*Munch. Med. Woch.*, 1906, No. 28) by the great variation in urinary secretion in animals, due to various factors such as quantity of food and water consumed, fecal excretion, and animal idiosyncrasy. The appearance of morphine in the stomach of a cat following hypodermic mesenteric injection is a matter of interest. Although only a small quantity is present its constant appearance is similar to the case of arsenic, which, irrespective of the mode of introduction, always appears in the stomach. The constancy of results in the spleen extraction is important, the spleen of all organs, in both cats and rabbits, being subject to least variation in morphine content.

The results of extraction from rabbits are subject to less fluctuation during the course of the experiments than with cats during the corresponding period. Arranged in order of morphine content the results rank as kidneys, liver, urine, spleen, and stomach. Rabbit "E" differed from the others in that it received a larger dose of morphine, and was not embalmed. That the urine contains the greatest quantity of morphine agrees entirely with

the results of Van Kaufmann-asser (*Biochem. Ztg.*, liv., 161), of Van Ryn (*Chem. Zent.*, 1908, [2], 174; *Pharm. Weekblad*, 1907, xlv., 1353), and of Dorencourt (*Comptes Rendus*, lvi., 1338), drawn from the analyses of rabbits killed with morphine.

TABLE I.—Data obtained from Experimental Results. Morphine in the Organs of Cats, as gm. Morphine Sulphate.

	Cat A.	Cat B.	Cat C.
	Grm.	Grm.	Grm.
Kidneys	0.040	0.032	0.027
Liver	0.055	0.057	0.042
Spleen	0.031	0.023	0.020
Stomach	0.005	0.002	0.005
Urine	0.064	0.031	0.043
Total found	0.195	0.145	0.137
Total injected	0.200	0.200	0.200
Percentage found ..	97.5	72.5	68.5
Length of burial ..	Analysis started immediately after death.		
		One month.	Three months.

TABLE II.—Morphine in the Organs of Rabbits as gm. Morphine Sulphate.

Rabbit	A.	B.	C.	D.	E.
	Grm.	Grm.	Grm.	Grm.	Grm.
Kidneys	0.0757	0.0654	0.0621	0.0473	0.0111
Liver	0.0601	0.0580	0.0574	0.0437	0.0214
Spleen	0.0122	0.0121	0.0120	0.0101	0.0343
Stomach	0.0060	0.0057	0.0052	0.0045	0.0072
Urine	0.0340	0.0304	0.0314	0.0311	0.0421
Total found	0.1889	0.1716	0.1681	0.1367	0.1161
Total injected	0.2000	0.2000	0.2000	0.2000	0.5000
Percentage found ..	94.5	89.8	84	68.4	23
Length of burial—					
--Analysis started	Imme-	Two	Four	Six	Eight
	diately	weeks.	weeks.	weeks.	weeks.
	after	after	after	after	Unem-
	death.	death.	death.	death.	balmed.

Qualitative analyses of the tissues surrounding the organs examined giving uniformly negative results, osmosis cannot account for the gradual decrease in morphine content. From the preceding results it would seem that upon introducing morphine into the organs used in these analyses, part of it combines with some cell constituent, forming a compound which is relatively more resistant to decomposition than is the uncombined morphine. Decomposition of the organ produces chemical compounds which break up the "free" morphine, but do not appreciably affect the "combined" morphine. This decomposition and removal of morphine produces the "preliminary drop" in morphine content observed.

The fairly constant results obtained between the close of this period and the beginning of the "secondary drop" represent the results of analyses made after the "free" morphine had been disintegrated, but before conditions were such that the "combined" morphine would be affected. This period of time is fairly constant for all the animals studied.

The gradual disintegration of the "combined" morphine, starting when conditions became favourable, would account for the "secondary" drop in morphine content. This decomposition would probably lead to complete removal from the body of all morphine as such.

This conclusion is best shown by the kidneys and liver, while the constant results for the spleen would seem to indicate that all the morphine deposited in that organ was present during decomposition as "combined" morphine, which began decomposition at the same time as the "combined" morphine of the other organs.

Summary.

From the preceding work the following conclusions may be drawn :—

1. By means of a five-hour extraction, and three extractions with ether in both acid and sodium hydroxide solution, Autenrieth's modification of the Stas-Otto process is capable of yielding 97·5 per cent of the morphine injected into an animal, if analysis be started very soon after death.

2. The presence of formaldehyde as embalming fluid has no appreciable effect upon the extraction results.

3. The loss of morphine from a cadaver proceeds in two stages, a preliminary drop due to the splitting up of the "free" morphine present, then a period during which the morphine content is fairly constant, followed by a secondary drop due to the splitting up of the "combined" morphine; i.e., that morphine which had combined with some cell constituent, thus escaping the preliminary decomposition.

4. The "secondary" decomposition is greatly retarded by embalming, although there seems to be no effect on preliminary disappearance.

5. Results of analyses of cats and rabbits which have received hypodermic injections of morphine, embalmed, and subsequently analysed, may be interpreted successfully by this theory of "combined" morphine.—*Journal of the American Chemical Society*, xxxviii., No. 9.

ON THE PREPARATION AND IONISATION OF THE DIALKYLPHOSPHORIC AND BENZENEDISULPHONIC ACIDS.*

By W. A. DRUSHEL and A. R. FELTY.

THE acids studied in this investigation are the lower dialkylphosphoric acids of the general type R_2HPO_4 , simple monobasic acids, and the three unsubstituted dibasic isomeric benzenedisulphonic acids of the formula $C_6H_4(SO_3H)_2$. Ionisation measurements of only one of the dialkylphosphoric acids have been reported in the literature (Van Hove, *Bull. Acad. Roy. Belg.*, 1909, 282).

Preparation of Materials.

(a) *The Dialkylphosphoric Acids and their Alkali Salts.*—For making conductivity measurements the free dialkylphosphoric acids and their sodium salts were used. The trialkylphosphates (Limpricht, *Ann. d. Chem.*, 1865, cxxxiv., 347) were prepared by the action of the proper sodium alcoholate upon phosphorus oxychloride in the presence of ether, according to the equation $3RONa + POCl_3 = R_3PO_4 + 3NaCl$. The precipitated sodium chloride was filtered off and washed with ether. The ether was distilled off from the filtrate, and the trialkylphosphate was recovered from the residue and purified by fractional distillation, using diminished pressure for the tripropyl phosphate. The trialkylphosphates were decomposed by concentrated aqueous barium hydroxide, and the barium tetra-alkyl phosphates were purified by crystallisation from water. The anhydrous barium salts, dried to constant weight, were decomposed by the theoretical amount of sulphuric acid, taking care to avoid an excess, and the aqueous acid solutions were exactly neutralised with pure sodium hydroxide. The aqueous solutions of the three dialkyl sodium phosphates were evaporated in platinum. The sodium salt of dimethylphosphoric acid was recrystallised and dried to constant weight at $110-120^\circ$. The sodium salts of the diethyl- and dipropylphosphoric acids could not be re-crystallised, but were prepared by evaporating their aqueous solutions in platinum and drying to constant weight at $140-150^\circ$. These two salts are hygroscopic and must be weighed from

weighing bottles. The three sodium dialkyl phosphates were made up in N/8 solutions for conductivity work.

The dimethyl-, diethyl-, and dipropylphosphoric acids were prepared for conductivity work by treating weighed amounts of the pure barium salts with the theoretical quantities of sulphuric acid and making up the solutions to the proper normality, verifying the normality of each solution by titration with standard sodium hydroxide. The dipropylphosphoric acid was also prepared from the sodium salt by adding the theoretical amount of sulphuric acid, evaporating the solution on the steam bath, and extracting the free acid from the residue with absolute alcohol; the alcoholic solution was diluted with water, concentrated in platinum on the steam-bath, and finally made up to the proper normality with distilled water. The solution was found to be free from sulphate, and its normality was checked up by making a titration with standard sodium hydroxide solution.

(b) *The Isomeric Benzenedisulphonic Acids and their Alkali Salts.*—For the preparation of these acids and their potassium salts methods were chosen which give each acid and its salt entirely free from the acid or salt of either of its two isomers. This is important in the present investigation, for in order to compare the strengths of the three isomeric benzenedisulphonic acids it is necessary that each acid should be prepared entirely free from its two isomers. The *m*-benzenedisulphonic acid is the only one of the acids prepared by the direct sulphonation of benzene. When benzene is sulphonated, benzenemonosulphonic, *m*-benzenedisulphonic, *s*-benzenetrisulphonic, and possibly—under special conditions—a little *p*-benzenedisulphonic acid may be formed; but by properly regulating the temperature and concentration of the sulphuric acid the only products are the monosulphonic acid, the *m*-disulphonic acid, a little excess of sulphuric acid, and a trace of benzene. The benzene was removed by water, the excess of sulphuric acid as barium sulphate, and the strongly acid aqueous filtrate was then converted to the potassium salt by exact neutralisation with potassium hydroxide or carbonate and evaporation to crystallisation. By a number of re-crystallisations the pure potassium *m*-benzenedisulphonate was obtained in good yield, the monosulphonate tending always to remain in the mother-liquor. Potassium *m*-benzenedisulphonate was readily converted into the pure acid by the following procedure:—The potassium salt was dried at $200-220^\circ$ to remove the molecule of water of crystallisation, and the anhydrous salt was then mixed with the theoretical amount of powdered phosphorus pentachloride and warmed. After the reaction was over, the mixture was treated with cold water to remove the sodium chloride formed in the reaction, the insoluble diacid chloride was filtered off, dried, and purified by re-crystallisation from ether. The diacid chloride was obtained in quantitative yield, and was converted to the acid by heating for an hour with distilled water. This acid solution was then treated with a little more than the theoretical amount of pure silver oxide necessary to remove the hydrochloric acid formed in the hydrolysis. Care was exercised in preparing the silver oxide to wash it thoroughly and repeatedly with boiling distilled water in order to remove every trace of alkali and sodium nitrate resulting from the precipitation of the silver oxide by the action of sodium hydroxide upon a dilute hot solution of silver nitrate. The free disulphonic acid containing a little silver disulphonate was separated by filtration from the silver chloride and treated with hydrogen sulphide in excess. The precipitated silver sulphide was filtered off and the filtrate heated to boiling to remove the excess of hydrogen sulphide. The solution was tested for silver and for halogen, and was found to be free from both. It was an aqueous solution of pure *m*-benzenedisulphonic acid of about N/5 concentration. The solution was standardised against decinormal sodium hydroxide and then diluted with freshly distilled water to N/8 concentration for beginning the conductivity measurements.

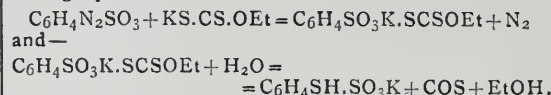
For the introduction of the sulphonic acid group, SO_3H ,

* From the *American Journal of Science*, xliii., p. 57.

into the benzene ring in positions other than meta to acid groups already in the ring, several methods have been proposed. P. Klason (*Ber.*, 1887, xx., 350) acted upon the diazo salt of sulphanilic acid with alcoholic potassium sulphide to introduce sulphur in the para-position to the sulphonic acid group. He obtained the potassium salt of *p*-thiophenolsulphonic acid, $\text{KSC}_6\text{H}_4\text{SO}_3\text{K}$ 1.4, which on oxidation with potassium permanganate gave potassium *p*-benzenedisulphonate. C. J. Blanksma (*Rec. Trav. Chim. Pays-Bas*, 1910, xix., 111) and J. J. Polak (*Ibid.*, 1910, xxix., 419) prepared the ortho- and para-nitrobenzenedisulphides by the action of sodium disulphide upon the corresponding chloronitrobenzenes. These disulphides, $\text{NO}_2\text{C}_6\text{H}_4\text{S}\cdot\text{SC}_6\text{H}_4\text{NO}_2$, on oxidation gave the corresponding nitrobenzenesulphonic acids, $\text{C}_6\text{H}_4\text{NO}_2\cdot\text{SO}_3\text{H}$. In 1890 the xanthate method of R. Leuckart was published (*Journ. Prakt. Chem.*, 1890, xli., 179). This was shown by Ehrhardt (*Journ. Prakt. Chem.*, 1890, xli., 184), Ruhnuu (*Ibid.*, 1890, xli., 184), and others to be a general method of preparing various sulphonic acids free from their isomers. Polak (*loc. cit.*), Walter (*Proc. Chem. Soc.*, 1895, xi., 141), and Armstrong and Worley (*Proc. Roy. Soc.*, 1914, xc., 86) used this method for the preparation of *o*- and *p*-benzenedisulphonic acids. None of these investigators, however, described the xanthate method with sufficient particularity to make a fair yield of the disulphonic acids possible without further experimentation. Since the disulphonic acids can be obtained entirely free from their isomers, it was deemed desirable to determine more closely the conditions which give the best yield of these acids. The xanthate method uses as starting out material in each the corresponding amidobenzenesulphonic acid, and involves the following steps to obtain the potassium salt of the benzenedisulphonic acid:—(1) Diazotisation of the amidosulphonic acid; (2) action of the diazo-compound with potassium xanthate to form the xanthate ester; (3) hydrolysis of the xanthate ester to form the potassium salt of thiophenolsulphonic acid, and its oxidation to the disulphide of potassium benzenedisulphonate; and, finally, (4) oxidation of the disulphide to potassium benzenedisulphonate by means of potassium permanganate. The steps and conditions for the formation of the potassium *o*- and *p*-benzenedisulphonates are essentially the same, starting with *o*- and *p*-amidobenzenesulphonic acids.

Several points are of importance in carrying out the processes previously mentioned. Diazotisation of the amidobenzenesulphonic acids by passing N_2O_3 gas through a suspension of the amidosulphonic acids in cold water is unsatisfactory, since the amidobenzenesulphonic acids as well as their diazo-compounds are only slightly soluble in cold water, and an attempt to diazotise in this way results merely in the superficial diazotisation of the solid particles, and rarely results in the diazotisation of more than 20 per cent of the amidobenzenesulphonic acid, even after passing the N_2O_3 for several hours. The most satisfactory method proved to be a slight modification of Fischer's process. The amidosulphonic acid was treated with about an equal weight of water, and to this was added a cold saturated solution of the theoretical amount of sodium nitrite, resulting in immediate diazotisation with evolution of heat, probably according to the equation $\text{C}_6\text{H}_4\text{NH}_2\cdot\text{SO}_3\text{H} + \text{NaNO}_2 = \text{C}_6\text{H}_4\text{N}_2\text{OH}\cdot\text{SO}_3\text{Na} + \text{H}_2\text{O}$. The mixture was at once treated at room temperature with the calculated amount of concentrated hydrochloric acid, with stirring. Reaction took place at once with the separation of the diazo-compound, $\text{C}_6\text{H}_4\text{N}_2\text{OH}\cdot\text{SO}_3\text{Na} + \text{HCl} = \text{C}_6\text{H}_4\text{N}_2\text{SO}_3 + \text{NaCl} + \text{H}_2\text{O}$. To make the separation of the diazo-compound as complete as possible the mixture was chilled in an ice-bath, then quickly filtered on a porcelain funnel with suction, and washed with a little ice-water. The diazo-compound was made into a thin mush with water and added in small portions to the calculated amount of potassium xanthate dissolved in about ten times its weight of water and heated on the steam-bath to 65° or 70°. Vigorous reaction took

place at once with copious evolution of nitrogen after the addition of each portion of diazo-compound. At the temperature used the xanthate ester formed was immediately hydrolysed chiefly to the corresponding thiophenolsulphonate. These reactions may be expressed by the following equations:—



Hydrolysis was completed by evaporating the reaction mixture to dryness on the steam-bath, during which process the thiophenolsulphonate was oxidised by the air chiefly to the disulphide, $\text{KSO}_3\text{C}_6\text{H}_4\text{S}\cdot\text{SC}_6\text{H}_4\text{SO}_3\text{K}$.

The disulphide prepared as described always contained an orange-red dye resulting from the diazo-reaction. This dye is soluble in alcohol while the disulphide is not. The disulphide was therefore purified from the dye by twice precipitating the disulphide from its saturated aqueous solution by the addition of alcohol. The trace of colour still remaining could be removed later by means of animal charcoal. On oxidation the disulphide yields the corresponding benzenedisulphonate. The oxidation was best effected by the use of hot saturated aqueous potassium permanganate, which was added in about theoretical amount in small portions in the course of twenty to thirty minutes to the cold dilute aqueous solution of the disulphide. The reaction evolved considerable heat, but the temperature was not at any time allowed to rise above 60°. Toward the end of the oxidation the solution retained the purple colour of the permanganate for ten to fifteen minutes on the steam-bath. This slight excess of permanganate was finally destroyed by the addition of a few drops of alcohol. The reaction mixture was somewhat diluted by the addition of water and allowed to stand on the steam-bath until the hydrated oxide of manganese had well settled out. The oxide of manganese was then easily removed by filtration with suction, and was well washed with hot water on the porcelain funnel. The combined filtrates were concentrated on the steam-bath to crystallisation and allowed to stand over night for the potassium benzenedisulphonate to crystallise out. If any of the reddish dye persisted at this stage it was removed by animal charcoal. The *p*-benzenedisulphonate was further purified by re-crystallisation from water. A 60 per cent yield of potassium *p*-benzenedisulphonate may be obtained from sulphanilic acid by the xanthate process under favourable conditions. A convenient method for the purification of the *o*-benzenedisulphonic acid is to convert the potassium salt into the barium salt by the action of saturated aqueous barium chloride and re-crystallisation of the barium salt from hot water. This method was described by J. J. Polak (*Rec. Trav. Chim. Pays-Bas*, 1910, xxix., 418).

The *o*-benzenedisulphonic acid was prepared from *o*-amidobenzenesulphonic acid by the xanthate method. The amidosulphonic not being obtainable in the market, it became necessary to prepare it in the laboratory. In its preparation from aniline a few important points must be observed in order to obtain the final product in pure condition and in good yield. Several modifications were introduced into the processes described in the literature, increasing the yield and improving the purity of the products. Parabromacetanilide was prepared from aniline by a modification of Hübner's method (*Ann. der Chem.*, 1881, ccix., 355). One mol. of aniline, one mol. of acetic anhydride, and two mols. of glacial acetic acid were mixed and allowed to stand until cold. To this mixture one mol. of bromine was added in small portions with cooling. When the last portion of bromine was added crystals began to separate out, and the mixture was immediately poured into a litre of cold water with stirring. On re-crystallising the precipitate from alcohol, snow white *p*-bromacetanilide was obtained in almost quantitative yield. The *p*-bromacetanilide was converted to *p*-bromaniline-*o*

sulphonic acid by heating at $170-180^{\circ}$ with the theoretical amount of sulphuric acid of specific gravity 2.0 in an oil-bath until the acetic acid was completely eliminated, instead of heating the mixture directly over a free flame as suggested by Kreis (*Ann. der Chem.*, 1895, cclxxvi., 377). In this way charring was entirely avoided and the yield was practically quantitative. The method of removing the bromine from *p*-bromaniline *o*-sulphonic acid suggested by Kreis was also modified in an important point, shortening the time required and improving the quality of the product. Under the conditions described by Kreis, boiling with zinc dust in alkaline solution for nine hours was found insufficient to remove completely the bromine from 60 grms. of *p*-bromaniline-*o*-sulphonic acid. A 60 gm. portion of this sulphonic acid was boiled for three hours with 600 cc. of sodium hydroxide solution containing 15 grms. excess of sodium hydroxide and 25 grms. of zinc dust. At the end of three hours a titration of 5 cc. of the solution showed that over 70 per cent of the bromine had been removed from the benzene ring. Fifteen grms. more of sodium hydroxide and 10 grms. of zinc dust were now added and the boiling continued for two and a-half hours, when a titration showed that the bromine was removed quantitatively from the benzene ring. In other particulars the method was carried out as described by Kreis, obtaining a good yield of pure *o*-amidobenzenesulphonic acid.

The *p*-benzenedisulphonic acid was prepared from its purified potassium salt by the procedure described for the *m*-benzenedisulphonic acid. The *o*-benzenedisulphonic acid was prepared directly from its purified barium salt by the action of the theoretical amount of sulphuric acid. The purity of the three disulphonic acids was determined by converting portions of their purified potassium salts into the acid chlorides and taking the melting-points of the acid chlorides (ortho- 143° , meta- 63° , para- 139°) re-crystallised from ether, and by converting the acid chlorides to the acid amides and taking their melting-points. For beginning conductivity measurements the three isomeric disulphonic acids were made up in N/8 solutions with freshly-distilled water, and for the determination of the strengths of the acids as catalytic agents in the hydrolysis of ethyl acetate they were made up in N/10 solutions. The normality of the acids was checked up in every case by making titrations with standard sodium hydroxide.

(To be continued).

THE TRAINING OF THE WORKS CHEMIST IN PHYSICS.*

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IN any works in which the value of scientific methods is recognised, the duties of the works chemist are important and varied in character; and the wider his range of knowledge, the more useful is he likely to become to the establishment. Amongst the subjects which must form a part of his mental equipment, that of Physics is one of the most important, and in particular the branches of light, heat, and electricity. It is the purpose of this paper to give an account of the course of instruction in Physics at the City and Guilds Technical College, Finsbury, at which institution students in the chemical department are trained with the definite view of fitting them for entry into works as chemists. Judged by results, the course has proved satisfactory; and in view of the greater importance which it is hoped will be attached to the works chemist in the future, a description of the chief features may prove of general interest.

In training a student for any industrial pursuit, it must

be remembered that the object of a works is to make a profit, and that the value of a man to the establishment is gauged by the extent to which he contributes to those profits. High scholastic attainments are of no value to a works unless they can be applied profitably to the work upon which the firm is engaged. Much indignation has been recently expressed at the low salaries offered by various firms to men who had obtained a university degree; but the fact is that the training necessary to obtain a degree may not qualify a man to be immediately useful in a works. Although it is not possible to draw a hard and fast line between "pure" and "applied" science, there is a vast difference between laboratory work and successful production on a commercial scale, and a man highly skilled in the former may not possess the aptitude for the latter. If a student is to be useful in a works immediately on leaving college, he must be to some extent familiar with works practice and procedure, and particularly must have a knowledge of the applications of science to the industry he enters. The unfortunate lack of co-ordination between science and industry in this country has been largely due to the fact that the industrial side of science has been neglected by the universities and colleges, and the type of student turned out has not been suited to commercial work. Owing to the birth of the modern universities, the growth of technical colleges and schools, and the realisation by employers generally of the importance of scientific methods, the outlook is now more favourable; but if a permanently better state of things is to result, it will be necessary for the colleges to provide the employer with a really useful type of man. It therefore behoves all teachers of technical science to work towards this end in the branch in which they are engaged, and to co-operate with their colleagues in order to secure the best results.

The general plan which, in my opinion, should govern the whole college training of a works chemist should consist primarily of a sound teaching of fundamental principles, accompanied with or followed by instruction in the industrial applications of those principles. No college can turn out a finished works chemist, any more than a finished engineer; but what it can do is to produce a type of man who possesses the requisite kind of information, the right outlook, and a degree of manipulative skill. It is often difficult to decide the correct proportions between the theoretical and technical parts of the instruction, and it is here that the experience of the teacher, guided by the calibre of the students, must be relied upon. It is unwise to give too great a preponderance to the purely technical side, as this leads to a restricted outlook; and it must always be remembered that what is merely a scientific curiosity to-day may lead to a great industry in the future. I have always found, however, that a study of practical applications is the best method of impressing the principles on the mind of the student, and invariably leads to a keener interest in the subject. It sets his thoughts on the right track, and serves as a fitting prelude to his commercial career.

Coming to the specific type of instruction given in Physics at the Finsbury Technical College, it is arranged that physico-chemical subjects, such as electro-chemistry, osmotic pressure, &c., are dealt with in the chemical department, either following or parallel with the instruction in sound, light, heat, and electricity imparted by the Applied Physics staff. The dove-tailing of the subjects between the two departments is convenient, and avoids overlapping. Taken over the three years which constitute the full chemical course, the student receives approximately one hundred and twenty lectures in purely physical subjects, and spends about two hundred hours in the laboratories. A certain school of educational "reformers" have attempted to belittle the value of the experimental lecture, and have proposed to substitute for it a kind of advanced kindergarten, which is supposed to train the students in methods of thinking. Long experience has convinced me that the experimental lecture is indis-

* A Contribution to a General Discussion on "The Training and Work of the Chemical Engineer," held by the Faraday Society, March 6, 1917.

pensable in higher-class teaching, and especially so when time is limited. It may be made the medium of instruction in correct methods of scientific reasoning; but at the same time students in early manhood should be given something to think about. In our laboratories the students are permitted to use the best apparatus procurable with the funds at disposal, and do not waste time in constructing makeshift appliances which at best give only approximate results. In a works the chemist will have to use good class instruments, and the sooner he becomes accustomed to handling them the better. The laboratory work, as far as possible, is made complementary to the instruction given in the lectures, but in point of time is mainly devoted to heat and electricity.

The utilitarian value of the subject of sound in the training of a works chemist might appear to be open to question; but the advantage lies in the fact that ideas of waves, vibrations, and harmonic motion, which are of wide application, are best presented through the medium of this subject. Even if this was not the case, it would still be advisable, from the standpoint of furnishing the student with a broad basis of general knowledge, to include sound in the curriculum. Ideas gathered in connection with acoustical experiments might give a clue to the solution of a problem in an entirely different sphere; and my personal impression is that it would be a mistake to abolish the teaching of sound to technical students. About twelve lectures are devoted to this subject at Finsbury, but no time is available for laboratory work.

The importance of a knowledge of light to the works chemist will be generally admitted. He may have to deal with microscopes, refractometers, polarimeters, optical pyrometers, &c., and may often need to devise optical arrangements for special purposes. The lectures in this subject are not confined to the principles of reflexion, refraction, dispersion, polarisation, and photometry, but extend to a description of the optical instruments used in the industries. During his period of training, the student has an opportunity of using a number of these instruments in connection with his chemical or other laboratory work, and thus becomes acquainted with their adjustments and possibilities. A certain amount of laboratory work in connection with lenses, mirrors, and prisms is carried out with a view to helping the student to a proper understanding of optical apparatus, but these are dispensed with when—as is frequently the case—the students have performed the experiments before joining the college. The practical work in light therefore largely consists in working with instruments, using them for the purpose for which they were intended.

A large portion of the Physics syllabus is devoted to heat, as the industrial applications of this subject are more numerous than in the case with any other branch. In the lectures the principal divisions, such as expansion, vapours, radiation, &c., are all illustrated by reference to practical appliances. As an example, in dealing with expansion, such devices as fire-alarms, steam-traps, &c., are explained, and the properties of non-expansive bodies such as invar and vitreous silica described, together with their special uses. The advantage of proceeding on these lines in the case of students intended for industrial life is evident after a few lectures, as a healthy spirit of inquiry is set up, and the student begins to look out for similar things in other directions. After treating the subject under the usual headings in this manner, special lectures are given on subjects which cannot be placed in any single division, but which are of the greatest importance. One set of lectures is devoted to fuels and their uses (and here I may remark in parenthesis that it is an inexplicable mystery to me why practically all text-books on heat carefully avoid all mention of fuels). Electrical methods of producing heat are also dealt with, and compared with fuel heating from the standpoints of temperature and cost. In relation to the subject of fusion, special attention is given to materials of high melting-points and their uses, including an account of refractory materials; and in the same con-

nection the fundamentals of the thermal analysis of alloys are explained. A special feature is made of the subject of pyrometry, which is daily growing in importance, and which should form a part of the curriculum of every technical institution in which students are trained. It is now twelve years since, in conjunction with the late Dr. Silvanus P. Thompson, I introduced a course of instruction in pyrometry, treating the subject not merely from the standpoint of measuring a temperature and obtaining a figure, but also from that of the industrial utility of pyrometers, and dealing with the advantages, special uses, and limitations of each type. There are few subjects better fitted to the dual purpose of emphasising scientific principles and imparting useful knowledge to the works chemist; and the only complaint I have received regarding this subject is that it possesses a fascination for students, and tends to put them off their other work. Other matters specially dealt with are heat insulation, as an application of conduction; refrigerating machinery in connection with the production of low temperatures; and the efficiency of engines as an example of the relation between heat and work. The idea which it is endeavoured to convey in the whole of this work is that the subject is not merely a matter of figures and formulæ, but something which will crop up daily when the student enters industrial life.

The laboratory work in heat embraces the determination of the various thermal constants of materials, such as coefficients of expansion, specific heats, &c., which are useful in training the student in experimental methods; and in addition practical work is given in pyrometry, fuels, thermal conductivity, and the use of electric furnaces. In all cases the student is permitted to use the best instruments available—which are frequently identical with those used in works—and in this way receives direct training in his future calling.

In any modern works the chemist is sure to come into contact with some electrical process or apparatus, and accordingly he is made to attend a course of lectures which deal first of all with the principles of electricity, and afterwards with measuring instruments, illumination, dynamos, motors, and accumulators. In the laboratory he conducts experiments designed to teach the arrangements of circuits; the measurement of pressure, current, and resistance; and the precautions necessary in using power from mains. Here again he uses the same kind of instruments—ammeters, voltmeters, &c.—as will be found in works, and is thus introduced to an important branch of his future duties.

In addition to lectures and laboratory work, a number of exercise classes are held, at which numerical examples relating to the various subjects are worked out. Some of the exercises given refer to practical problems, such as the fuel costs in prime movers for a given power production; or the deduction of conclusions from the figures obtained in an overall test of a steam-engine plant. These classes are found to be a valuable aid to the general instruction.

The course in Physics here outlined is general in character, and in the case of students intended for special industries might be amplified in certain directions to suit the circumstances. For example, if the student were entering a steel works, a course in micrography would be an advantage, and similarly more extended work on colours would be desirable for one joining the dyeing industry. Special work of this kind is best carried out at institutions located in the centre of the industries concerned; but in all cases the instruction should embrace the subjects referred to in the present paper if a really competent man is to be produced. It is very important that the instruction should be kept up to date, and this means that the teacher must keep in touch with the progress of science, both pure and applied. Whenever possible, the students should be encouraged to attend meetings of societies when subjects relating to their work are under discussion—as, for example, the conferences on refractories, &c., held by this

Society—so as to get into touch with modern progress. The chemist who is to be of the maximum use to his employer must, in addition to the possession of specific knowledge, have his ideas running in the right grooves.

Since the outbreak of the war manufacturers in this country have been severely attacked for their backwardness in connection with research, largely by literary individuals who are ignorant of what research implies. Admitting that some—but by no means all or even the most important—of our industrial men have been remiss in this direction, it is equally true that most of our scientific men have held aloof from research of a commercial character. What can be achieved by a combination of skilled scientific men and wideawake commercial men is illustrated by the work of our National Physical Laboratory. At present more reputation is to be gained by research in “pure” science; but when we come to a just recognition of values, and realise that the discovery of a new process which adds to our commerce is equal in importance to measuring the length of the tail of a comet, then we may expect our best scientific men to give some of their attention to industrial research. It is their detachment which, in no small measure, has led to the common belief that science is something apart from daily activities, and thence to the low esteem in which trained science students are held, and the generally low remuneration they receive.

I have introduced this matter as the inquiry might reasonably be made: “What provision is made for research in the course of Physics recommended?” In general, it may be answered that until the student has secured a good hold of the subject he is not fitted to conduct a research on his own account. Opportunity is frequently afforded, however, for specially capable students to participate in researches which are being carried out by members of the staff, and a spirit of inquiry is fostered throughout. When an investigation has been completed and published by one of the staff, it is customary to give an account of it to the students, explaining how the various points were led up to, and showing the actual apparatus used. It is not possible to teach research; all that can be done is to impress its value and to indicate methods. After leaving college only a portion of the students, who possess what might be called the “research temperament,” may be expected to devote time to original investigations in connection with the development of scientific knowledge. All who have taken full advantage of their instruction, however, should be able to deal successfully with the problems that arise in industrial practice; and it is to assist in achieving this end that the course in Physics herein described is designed. Many years of experience have proved its value, and it is hoped that the details may prove of service to those interested in the important matter of the proper training of the works chemist.

A PLEA FOR THE FORGOTTEN FACTOR IN CHEMICAL TRAINING.*

By W. R. COOPER, M.A., B.Sc.

In considering the training of the chemical engineer nine people out of ten (and even more) take the view that so long as the student at the end of his course has a good knowledge of theoretical chemistry and laboratory methods, and has some notion of the main manufacturing processes, as disclosed by text-books, his training is complete. If he has passed through one of the few laboratories where commercial processes entering into manufacture may be studied, so much the better.

It is, of course, true that no manufacturing concern can be thoroughly and permanently successful unless its

technical processes are fully understood. The technical aspect is therefore always emphasised. Yet, however perfectly the theoretical and technical knowledge of the young chemist may be developed during his technical training, there is usually an all-important factor which is wholly neglected, namely, £ s. d. In other words, will any particular process pay? Of course this question is very unscientific, and I feel I must almost apologise for bringing it before a scientific society; but the fact remains that the end and aim of every commercial chemical process is to make a profit or to reduce a loss (which is really the same thing), and yet this all-important point of view is omitted from the student's course.

If cost could be disregarded the power of the scientific man would be much increased. Unfortunately, results obtained regardless of cost are of no commercial value. In days to come it may well be that one of our chemists will discover the transmutation of lead into gold, and the daily Press will forthwith assure their readers that, as soon as this memorable discovery can be put to work, gold will be comparatively worthless, because a hundredweight of lead costs much less than an ounce of gold. But in all probability Nature has so adjusted the elements that an ounce of transmuted lead will cost a good deal more than an ounce of gold as obtained by present-day methods, when all the charges are taken into account. The inclusion of all the charges is where the trouble comes in, and it is in this way that a competitive process frequently turns out to be much less formidable than was anticipated by its promoters.

The idea of introducing the factor of cost is often distasteful to the teacher, probably in proportion to his academic attainments; but to imagine that a commercial problem is on a lower plane than one that is purely scientific is a mistake, for it includes the additional factor of cost, which makes it all the more difficult of solution. The methods used may be less refined and less accurate, but that is only a matter of degree. Moreover, the probability is that the working on a commercial scale introduces complications which in the laboratory were not apparent, and thus there are fresh fields of difficulty unforeseen by the academic worker.

A few points may be mentioned by way of illustration.

A fundamental characteristic of any stable commercial enterprise is that it should be run at a profit. This is a truism, and yet, as a rule, the young chemical engineer has the haziest notion of what is meant by profit. He generally thinks that so long as the price obtained exceeds the cost of material and labour, together with a small margin towards rent and management, a profit is being made. This, of course, is far from the case.

It seems desirable that there should be some appreciation of the fact that manufacturing cost, even when correctly determined, is only one part of the total. The cost of selling the product is equally important, and in some cases is much greater than the cost of manufacture. In the first few years of an enterprise this may be particularly important.

Then there is the question of the depreciation of plant, which may be very heavy under certain conditions, and the kindred problem of obsolescence. The latter may be forced upon the user through the medium of competition, it being found that an old type of plant must be discarded in favour of a newer type if the costs are to be reduced to meet competition.

Further, there is the division of costs into “overhead” and running costs, the former being the costs which are incurred simply by being ready to manufacture and to sell, apart from the cost of actual production. The overhead cost as a total per annum is fixed for the time being, and thus the extreme importance of a maximum output for a given overhead cost per annum is seen if the cost of the product is to be a minimum. This means that the full utilisation of plant (*i.e.*, of capital) is vital, and may necessitate the employment of more than one shift.

With this part of the subject is bound up the question

* A contribution to a General Discussion on “The Training and Work of the Chemical Engineer,” held by the Faraday Society, March 6, 1917.

of the utility factor or commercial efficiency of plant as distinct from technical efficiency. The technical efficiency of a plant when at work may be quite high; in other words, the waste of materials or of energy in obtaining the product may be small. Yet, if it is necessary to interrupt the working of plant for discharging, charging, adjustment, &c., the utility factor (*i.e.*, the ratio of the quantity of material actually produced during, say, a year to the quantity that would be produced if the plant were working continuously under the best conditions) may be low. It may be worth while to have a lower technical efficiency if this increases the utility factor, and it is on these lines that the merits or continuous *versus* discontinuous processes must be weighed.

An equally important point in many cases, but one which may not be appreciated by the young chemist, is the speed at which a reaction will take place. Take, for instance, the case of a catalytic process. If the speed of reaction can be doubled, this may make all the difference between success and failure commercially, owing to the difference in the capital required, or it may enable the manufacturer who secures this end by investigation to compete more readily with other manufacturers.

The above points will serve as a few examples to illustrate what I mean by the "forgotten factor." By some it is urged that such matters should receive no attention in our educational courses; that the would-be chemical engineer should study merely chemistry, theoretical and applied. The view is taken that if the student is well grounded in this way he will soon pick up the rest when he enters the works, assuming that the need ever arises for such knowledge. In the case of large works this may be true enough; the young chemist may possibly not come across the commercial side at all, and when he does so he will find himself among those who already have sound views on commercial efficiency. But in small works and in other lines of activity this is often not the case; the young chemist may find himself without such guidance, and may nevertheless be called upon to decide or advise upon processes on broad commercial lines. It therefore seems a mistake to leave the profit side of chemical operations entirely untouched. I feel that if this aspect were impressed upon the young chemist we should not so often see the spectacle of unsound chemical processes being put forward by the chemist, and even backed by men of the highest repute in the world of chemistry. They would realise that there is much to be considered beyond the fundamental chemical reactions of a given process.

Something, though not much, is being done by our modern universities to deal with commercial matters. For example, Birmingham University has established a Faculty of Commerce. One of the two alternatives presented by the syllabus is for the benefit of students who expect to be engaged in the commercial conduct of manufacturing businesses, and such students are permitted to devote about one-third of their time to the study of applied science. For a commercial training this division of time would, no doubt, be satisfactory, but would, of course, be quite in the wrong proportion for the chemical engineer. Actually, as far as I am aware, nothing is done by our schools at present to meet the case here considered.

It is generally recognised that any serious prolongation of, say, a four years' course is undesirable. It appears to me, however, that this would not be necessary to secure the desired end. What is required is a grounding in sound principles rather than an acquaintance with much detail, and probably this could be accomplished without difficulty in a course of three months at the conclusion of the technical course. Undoubtedly there are many other subjects of which some knowledge is desirable, such as works organisation, methods of remuneration, economics, and the law of contracts, but these can be left more readily for the student to consider when they are forced upon him.

In conclusion, let me say that while I do not suggest any very drastic alteration in our methods, I do put for-

ward a strong plea for the consideration of the one factor which is generally omitted from every college training, but which, nevertheless, regulates our attitude towards every process in commercial working.

PERCIVAL LOWELL.

By FRANK W. VERY.

ASTRONOMY has suffered a severe loss by the sudden death of the distinguished American astronomer, Percival Lowell, which occurred at Flagstaff, Arizona, on Sunday, November 12, 1916. To those who have had the privilege of listening to Dr. Lowell's lucid expositions of those great astronomical discoveries in which he had a part, the news will come with a sense of keen personal loss. He always took his audience with him into an inmost intimacy, showed his hearers science in the making, gave a human interest to everything he touched, and by the brilliancy of his faultless diction and his keen but kindly wit, fairly took them by storm.

The clever *bon mots* of a popular lecturer will not always stand the severe scrutiny of a drier and more rigid scientific criticism, but if anyone supposes that Dr. Lowell was a mere maker of happy phrases, he has missed the real genius of the man. As a student at Harvard University, a notable future as a mathematician was foretold for him by his teacher, Benjamin Peirce. This prediction was easily fulfilled. Such papers as the "Memoir on a Trans-Neptunian Planet" bear witness to long years of industrious investigation in the difficult study of celestial mechanics, and though the actual detection of the body, or bodies (for there is some reason to suspect that there are two of them) did not reward the diligent search by Dr. Lowell and his assistants, there can be no doubt of the reality of the gravitational disturbance made known by the mathematical analysis.

Equally fertile in results requiring the highest sort of mathematical ability in their making, was the demonstration that Saturn has "confocal layers rotating faster within," founded upon the extraordinarily difficult observation, by Dr. Lowell and Mr. E. C. Slipher at Flagstaff, of excessively fine and delicate dark dividing lines in Saturn's rings, whose fixed positions were found to be attributable to the perturbations of Mimas and Enceladus, but with minute variations which could only be explained on the hypothesis of a yielding of the plastic interior of the planet, and a more rapid rotation of the inmost nucleus with resulting larger oblateness than that of the outer surface.

These achievements place Dr. Lowell's name high on the lists of those who have wrested secrets from nature by severe labour of mathematical and intellectual thought. But his chief fame will still be that, even more than Schiaparelli, who first discovered the Martian "canals," Lowell was the man who made the map of Mars, enriching it with a great number of delicate markings, and envolving from their patient and assiduous study in all their complex variations, a rational theory of their meaning, which challenges our admiration. And although this theory of the origin of the lines in vegetation, irrigated and made possible by a complicated system of engineering works, has taxed the credulity of some less highly imaginative people, no one can deny its possibility, and no one has ever attempted to suggest a more plausible explanation. It will go down in the history of science as one of the best examples of the exercise of the "scientific imagination."

Dr. Lowell was born in Boston, Massachusetts, March 13, 1855. His father, Augustus Lowell, was much interested in education, and was for a long time a trustee of the unique "Lowell Institute," founded in Boston, in 1836, by a kinsman, John Lowell, jun. Augustus Lowell was also prominent in the foundation and maintenance of the Massachusetts Institute of Technology, where his on,

Percival, was afterwards for fourteen years, non-resident Professor of Astronomy. His mother was Katherine Bigelow (Lawrence) Lowell, daughter of Abbott Lawrence, who was Minister Plenipotentiary from the United States to Great Britain in 1851; and he was also related to the poet, James Russell Lowell, who later held the same position. On both sides, Dr. Lowell came from distinguished ancestry. He was very happily married to Constance (Keith) Lowell, but leaves no descendants.

The cities of Lawrence and Lowell on the Merrimac River, in Massachusetts, record the important place which the two ancestral families bore in the development of the cotton manufacturing industry, and Dr. Lowell, among his many other attainments, was a good business man, and served at one time as Acting Treasurer of the Massachusetts Cotton Mills, and Treasurer of the Lowell Bleachery, also as Director and Trustee of several other companies. Through his success as a business man, he was able to finance and found the great Observatory at Flagstaff, which bears his name. In his younger days he resided in Tokio, Japan, and returned to the United States as special Counsellor of the first embassy sent by Korea to a Western power. His residence in Japan and Korea gave him an insight into Oriental thought which bore fruit in such sympathetic studies as his "Chosun," published in 1885, "The Soul of the Far East" (1886), "Occult Japan" (1894), and this happy faculty of the literary man enriched all of his subsequent scientific writings, which included "Mars" (1895), "Annals of the Lowell Observatory," Vol. I. (1898), Vol. II. (1900), Vol. III. (1905), "Mars and its Canals" (1906), "Mars as the Abode of Life" (1909), "The Evolution of Worlds" (1910), and numerous scientific articles describing notable scientific discoveries in the "Bulletins" of the Lowell Observatory, in current scientific magazines, and in the Proceedings of Societies. He was made an Honorary Fellow of the Royal Astronomical Society of Canada, and received many other honorary recognitions of his distinguished services to science.

The work of the Observatory will be continued by the aid of a fund bequeathed by Dr. Lowell for this purpose, and by his wish the fund will be administered by his cousin, Guy Lowell, the architect of the New York Public Library, who was in full sympathy with him. The friends of Percival Lowell could ask for no more worthy memorial of him than the perpetuation of the work which he had at heart, and no better monument to his genius could be erected than the great observatory which he founded.—*Journal of the Royal Astronomical Society of Canada*, January, 1917.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, March 22, 1917.

Sir J. J. THOMSON, O.M., President, in the Chair.

PAPERS were read as follows:—

"Observations and Experiments on the Susceptibility and Immunity of Rats toward Jensen's Rat Sarcoma." By J. C. MOTTRAM, M.B., and S. RUSS, D.Sc.

Observations have been made upon the modes of growth of Jensen's rat sarcoma following inoculation. There is a gradual transition from those cases in which the tumours spontaneously disappear to those in which they grow in a uniformly progressive manner.

The spleens of animals exhibiting various grades of active immunity were examined, and it was found that a marked accumulation of lymphocytes and plasma cells occurs in the spleen of an animal which will not support the growth of the tumour. Intermixture of such spleen cells

and tumour cells before inoculation leads to a diminished growth of the latter.

The experimental production of the immune condition can be brought about in several ways. Animals made refractory to the growth of the tumour have been given various doses of X-rays; the effect of such irradiation upon the blood was to cause a marked reduction in the number of lymphocytes. Over suitable conditions of exposure it has been possible to destroy the immune condition, and thus convert refractory into tumour-bearing animals. There is a tendency for the immune condition to be restored.

Histological and other evidence is brought forward which indicates that the failure of sarcoma cells to grow in an immune animal is due to an active resistance thereto on the part of the host.

"Problems Bearing on Residual Affinity." By SPENCER PICKERING, F.R.S.

It has been ascertained that the alkali metals, like the other metals previously examined, form metallo compounds isomeric with normal salts, and that therefore these metals may assume a valency higher than that usually exhibited by them. A class of compounds intermediate between the metallo and normal salts also exists. These are termed metallato compounds. The possibility of most metals, other than carbon and hydrogen, assuming a valency value higher than that usually exhibited by them, is shown to explain (1) the constancy in the heat of substitution of CH_3 for H as contrasted with want of constancy in the case of the substitution of OH or Cl for H; (2) the fact that the heat of neutralisation of organic acids is lower than that of inorganic acids and exhibits certain distinctive features when only partially effected; (3) that all true acids must contain a doubly linked oxygen atom, and that the apparent exceptions to the constancy of the heat of neutralisation is due to the acid not being a true acid; (4) that the so called normal salts of the alkali metals with organic acids are strongly alkaline, and that those with inorganic acids are feebly so; (5) that the usual method of titration of an acid by an alkali, as well as the precipitation of the acid or base by usual methods, fails in the presence of an organic acid; (6) that the actual value of the heat of neutralisation constant can be explained.

"Residual Magnetism in Relation to Magnetic Shielding." By Prof. E. WILSON and Prof. J. W. NICHOLSON.

1. The paper contains a further contribution to the study of the problems presented by the necessity for constructing a magnetic shield capable of reducing the earth's field to an order as low as 0.001 C.G.S. units in a large space. The main problem not treated in earlier papers is that of residual magnetism in the various shells of the shield, and this problem is discussed in connection with exhaustive experiments in the present paper.

2. It is found that the ordinary process of demagnetisation of a mass of iron fails to be completely effective if, during the operation of the current which is diminished by steps and continually reversed, a constant magnetic field such as that of the earth is present at the same time. This phenomenon has escaped notice hitherto, probably on account of the smallness of the earth's field, but it becomes prominent in experimental work involving the measurement of fields so small as that specified in (1).

3. This effect of the steady magnetic field is shown to be associated with a reversal of the residual effects of hysteresis in iron when tested in the earth's field by currents lying within a certain range in which they approximately annul the field.

4. It has been found possible to ensure complete removal of the irregular polarisation or previous magnetic history of the shells, provided that during the preliminary demagnetisation of the shells the earth's steady field on them is annulled by a steady current of suitable amount enclosing the whole shield.

5. The well-known fact that iron, polarised by a large

force, and subsequently tested for permeability at a lower force, shows diminished permeability at the lower force, gives, in combination with these results, an interpretation of the increase of permeability manifested by iron when tested within a magnetic shield.

"The Solar and Lunar Diurnal Variations of Terrestrial Magnetism." By S. CHAPMAN, D.Sc.

CHEMICAL SOCIETY.

Ordinary Meeting, March 1, 1917.

Dr. ALEXANDER SCOTT, M.A., F.R.S., President,
in the Chair.

THE PRESIDENT referred to the loss sustained by the Society, through death, of the following Fellows:—John Griffiths and Cyril Douglas McCourt (killed in action); John Kent Crow, Reginald Le Neve Foster, Charles Henry Wood.

Messrs. S. C. Atkinson, C. E. Corfield, J. Dines, J. C. Johnson, H. King, J. Krizewsky, D. J. Matthews, and A. W. Richardson were formally admitted Fellows of the Chemical Society.

The names of Fellows recommended by the Council for election as Officers and as Ordinary Members of Council for 1917 to 1918 were read from the Chair.

Certificates were read for the first time in favour of Messrs. John Anderson, M.A., B.Sc., 5, Lintharthen Gardens, Dundee; Leon Daniel Goldsmith, B.Sc., A.R.C.S., 31, Colvestone Crescent, West Hackney, N.E.; Harold Pearson Hird, 3, Rock Terrace, Hipperholme, Halifax; George Samuel Mason, B.Sc., 28, Osborne Road, Birkby, Huddersfield; John Calvert Oxley, Oakwell House, Heckmondwike; Sydney Albert Pearman, B.Sc., 12, Stanley Gardens, Hampstead, N.W.; Alfred George Pollard, B.Sc., A.R.C.S., 27, Edburton Avenue, Brighton; George Reeves, B.Sc., A.R.C.S., care of British Dyes, Ltd., Dalton Works, Huddersfield; George Robertson, M.A., B.Sc., Mary Cottage, St. Andrews; Ernest Harry Rodd, D.Sc., A.C.G.I., 68, Clarence Road, Teddington; Oge Roewade, 214, Calhoun Street, Battle Creek, Mich., U.S.A.; William Smith, B.Sc., Mountsorrell, Loughborough; Robert Stevenson, A.P.O., S 14, B.E.F., France; Arthur Worthington, Lynwood, Great Lever, Bolton.

The following papers were read:—

"Notes on the Effect of Heat and Oxidation on Linseed Oil." By J. A. N. FRIEND.

"Acyl Derivatives of Paradiazoiminobenzene." By G. T. MORGAN and A. W. H. UPTON.

Ordinary Meeting, March 15, 1917.

Dr. ALEXANDER SCOTT, M.A., F.R.S., President,
in the Chair.

THE PRESIDENT referred to the death, on March 10, of Mr. Philip John Worsley, who was elected a Fellow on February 14, 1858.

Messrs. S. A. Brazier and H. C. Cocks were formally admitted Fellows of the Chemical Society.

Certificates were read for the first time in favour of Messrs. Charles Claude Carpenter, South Metropolitan Gas Co., 709, Old Kent Road, S.E. 15; Herbert Edwin Course, Water Works, Accra, Gold Coast; Major Percy Cowell, Royal Automobile Club, Pall Mall, S.W. 1; Arthur Charles Hoare, 63, Englewood Road, Clapham Common, S.W. 4.

A certificate has been authorised by the Council under By-law I, Par. 3, in favour of Vetscheslav Engenievitch Tschitschenko, Petrograd, Russia.

Mr. A. CHASTON CHAPMAN delivered a lecture entitled, "Some Main Lines of Advance in the Domain of Modern Analytical Chemistry," and illustrated it by experiments. A vote of thanks to Mr. Chapman for his lecture was moved from the Chair and carried with acclamation.

CORRESPONDENCE.

BLINDED SOLDIERS' AND SAILORS' HOSTEL.

To the Editor of the Chemical News.

SIR,—I hope you will be able to find room in your columns for the enclosed short appeal to members of the chemical trade. If you will permit the letter to appear you will, I know, be doing a great deal to help the men who have given their sight for the Empire.—Yours faithfully,
ARTHUR PEARSON.

Will you permit me to ask your readers if they will be so generous as to give support by gifts in cash or kind to the Blinded Soldiers' Bazaar, which is to be held at the Royal Albert Hall during the second week in May.

I feel sure that no flowery phrases are needed to evoke their sympathy for the men who have made so great a sacrifice for the freedom and future prosperity of this country.

So may I please just leave the matter like this:—

If you who read this letter think that the fight which Britain is making is a just fight, if you honour and respect the men who have represented you in that fight, if you have sympathy for those who in thus representing you have suffered so terrible a deprivation as the loss of their sight, you will send a contribution, be it large or small, be it in cash or kind, to the Secretary, Blinded Soldiers' Bazaar Committee, 6, Bayswater Hill, London, W.—I am, &c.,

ARTHUR PEARSON, Chairman,
Blinded Soldiers' and Sailors' Care Committee.

MISCELLANEOUS.

The Mersey Chemical Works, situated at Bromborough Port, New Ferry, Birkenhead, were sold by auction by Messrs. Wheatley Kirk, Price, and Co., of Manchester, on March 28. The property, which included frechold works premises, plant and machinery, electric light and power installation, was offered in one lot, and the bidding at the well-attended sale was brisk. The purchaser was Colonel Brotherton, of Messrs. Brotherton and Co., Leeds, Glasgow, and elsewhere, tar distillers, and the purchase price was £135,000.

TO comply with Regulation 8 (b) of the Defence of the Realm Act, advertisements from firms whose business consists wholly or mainly in Engineering, Shipbuilding, or the production of Munitions of War, or of substances required for the production thereof, must include the words "No person resident more than ten miles away or already engaged on Government work will be engaged."

Assistant Chemist required for large Engineering Works on North-East Coast. One familiar with the Analysis of Non-ferrous Alloys preferred. No person already engaged on Government work will be considered.—Apply, stating qualifications, age, salary, and when at liberty, to your nearest Employment Exchange, quoting No. A 3098.

Chemical Assistant, Junior (well qualified), wanted in a Laboratory in the East End of London.—Apply, with full particulars, to "Fumigant," care of Wilcox and Co., 26, Martin's Lane, Cannon Street, E.C. 4.

Situation wanted as Chemist or Assistant Manager. Metals, Minerals, Acids; Food and Drugs; Water Analyses; knowledge of Machinery. Silver badged from the Army.—Apply, Johnston, 174, Adelaide Road, S.E. 4.

Young Hollander, Chemical Engineer, Graduate of the Technical University at Delft, Holland, fully competent to act as Scientific Manager and to undertake responsible Laboratory Work; wants suitable Situation. First-class references.—Apply to "M G. 2438," Ricardo's Advertising Agency, Amsterdam, Holland.

Wanted, "MEMOIRS OF THE GOODWIN SANDS," by Mr. Gattie.—Address, W. S., CHEMICAL NEWS Office, 16, Newcastle Street, Farringdon Street, London, E.C. 4.

THE CHEMICAL NEWS.

VOL. CXV., No. 2994.

THE WORK OF THE IMPERIAL COLLEGE IN THE TRAINING OF CHEMICAL ENGINEERS.*

By J. W. HINCHLEY, A.R.S.M., Wh.Sc.

SOME years ago the Governors of the Imperial College of Science and Technology decided to establish a Department of Chemical Technology in which chemical engineering should form a section. A beginning was made with the teaching of chemical engineering in January, 1910, whilst Sir Edward Thorpe still occupied the Chair of Chemistry at the College, but the subject was not fully developed until it was definitely transferred to the new Department of Chemical Technology which was subsequently established in 1912 under the direction of Prof. W. A. Bone.

In 1912, when the Department of Chemical Technology was inaugurated, certain clearly defined principles were laid down for its development, which may be summarised as follows:—

1. The work of the department should be post graduate in character.

2. That no attempt should be made either to set up manufacturing plant on a small scale or to teach the actual practice of particular industries, but only to teach principles with illustrations drawn from practice.

3. That mechanical drawing, workshop practice, factory organisation and economics should form an integral part of the course.

It was decided in the first instance that the following branches of chemical technology should be included or provided for in the new department, namely:—(1) the technology of fuel and such cognate subjects as coal-tar and ammonia, explosives, and refractory materials; (2) chemical engineering, both of which have already been developed, to be followed as soon as circumstances permitted by (3) electrochemistry, and possibly (4) technical organic chemistry—fats, oils, glycerine, soap, starch, sugar, gums, &c.

In addition to the above subjects, lectures have been established in the principles of the manufacture of sulphuric acid, as a typical example of an inorganic chemical industry.

It will thus be seen that the subject of chemical engineering which is entrusted to me, under the general direction of Prof. Bone, as head of the department, is being developed in conjunction with, and as an integral part of, a larger scheme of post-graduate study and research in chemical technology.

During the summer vacation a selected number of students are enabled to pursue a month's course on a large works or experimental station, where they have opportunities for studying the conditions under which large scale operations are carried on.

The full-sized experimental gas producer plant which has been presented to the department by Mr. Robert Mond also affords opportunities for gaining experience in handling large plants, when experimental trials are made. It is fitted with devices by which the effects of variation in the "steam saturation temperature" and "superheat" of the air blast on the quality and yield of the gas may be accurately determined.

I do not propose, however, in this paper to direct attention to the lines on which the other sections of the

department—for which I am not directly responsible—are being developed, but I will confine myself to a few observations upon the principles which I consider ought to govern the teaching of chemical engineering as a post-graduate subject in a department of chemical technology.

I do not agree with Prof. Armstrong's recent declaration that the subjects of chemistry and engineering are antipodal in character, and that one should give up the notion of training chemical engineers and advise chemists and engineers to co-operate in chemical industry. Without saying one word against co-operation, it is my experience that all the chemical students, with two exceptions, who have taken the chemical engineering course at the Imperial College were most successful in the work of the course and may develop into excellent chemical engineers. One of the principles upon which the practical work of the course has developed is that it must involve *self-teaching* by the student himself, under adequate direction. The apparatus used must demand initiative in its erection and in its use, and the problems involved by the practical work must be similar and call for similar effort as those met with in industry.

A few of the features of the practical work may be mentioned as being suggestive. The student must compile a reference book from which he may at once obtain, without calculation, quantitative information on the subjects he has studied. One page of this book is covered with curves giving the properties of steam, the table from which they were drawn being on the opposite page; another page has curves showing the rate of evaporation from surfaces of liquids; another, the normal loss of heat by air contact and radiation from surfaces; another, the properties of mixtures of ammonia and water vapour (derived from Perman's work for ammonia plant design), and so on.

He is taught to use the most efficient methods of calculation, and is introduced to "utility" formulae.

He has to make himself familiar with methods of handling technical problems which are too involved for exact treatment, but are capable of determination within limits of practical accuracy.

He determines under conditions similar to those in factories coefficients to be used in designing. He makes drawings of simple units of plant—tanks, bins, stills, condensers, &c. He experimentally studies units of plant—filter-presses, reaction towers, wet and dry stills, grinding-mills, &c. He makes one or two original designs of simple plant for a given output of product, and finally studies one of several chemical processes on a scale adequate to bring out all the facts necessary for factory working. He designs the plant, prepares specifications and estimates, and determines the "cost of production" of the product. He also devises a system of factory records for the control of the plant, and also plans a factory for the manufacture.

This training cannot take the place of the factory, for it cannot give the wisdom obtained by experience, but it plants the "seed" which may grow to wisdom. An effort is made to instil good habits, for good factory habits are essential to commercial success, and too much care cannot be taken in cultivating and maintaining good methods and habits.

There is no doubt that after the war there will be a great demand for well-trained chemical engineers and technologists, and that the opportunities presented to properly qualified research chemists, with some knowledge and aptitude for industrial conditions, will be much greater and more attractive than ever.

This course is, I believe, providing students with an equipment and outlook which enables them to achieve immediate success in such practical undertakings.

* A Contribution to a General Discussion on "The Training and Work of the Chemical Engineer," held by the Faraday Society, March 6, 1917.

Written communications to the Discussion were received from—

Mr. G. S. ALBRIGHT (Ledbury), who, in emphasising the difference between laboratory work and works practice, pointed out that a more minute and careful study of *all the conditions* governing an experiment in the laboratory might save many mistakes outside. He was strongly impressed with the necessity to the chemist of some engineering knowledge, so that he should not be wholly at the mercy of the works engineer.

Mr. E. B. R. PRIDEAUX (University College, Nottingham)—The distinction between the research chemist and solver of technical problems on the one hand, and the works chemist or works manager on the other, seems particularly useful in discussing education for the profession of applied chemistry. It has been repeatedly emphasised at recent discussions on the present subject initiated by the Nottingham Section of the Society of Chemical Industry. The writer has in these discussions expressed an opinion that the students of the first kind may be sufficiently educated in institutions of university type with a relatively small equipment. The second kind, however, whose education is under discussion at the present meeting, may need to migrate to a large and highly equipped institution of the technical high school type. Since, however, this is sometimes impossible for the student, in practice institutions do their best to train all kinds of chemical students who may present themselves. It is important therefore to find out whether a smaller university with relatively slight resources can to any extent differentiate its courses to meet the somewhat different requirements of the works chemist, say, in a post-graduate year. In a recent paper before the British Association, Mr. F. H. Carr has outlined such a course. This might include a great deal of careful preparative work, especial attention being paid to purity of product, amount of yield, and the question of costs. Such a course, if worked in co-operation with local manufacturers, would probably enable the smaller universities to supply a sound training, not indeed for a chemical engineer, but for a most useful kind of works chemist. If properly conducted by an adequate staff of diverse qualifications it has still greater possibilities. For it would appear to involve almost necessarily the calculations of physical chemistry and a free application of the methods of practical physics and physical chemistry, and thus a constant co-operation between the physics and chemistry staffs. This seems to offer a way of making good some of the defects of our present system described by Prof. Donnan in *The Times Engineering Supplement* for July, 1916. It was stated there that "the only road to real applied chemistry lies through a close and thorough study of physical chemistry." The road of course lies through many other regions, and notably through that intimate knowledge of molecular reactivity which constitutes part of the skill of the synthetic organic chemist. But leaving the relatively more complex cases in which this chemical insight is at present so much more powerful than the calculations of chemical thermodynamics, it is easy to see how important it is that the young technical chemist should be able to use the latter also, for example, in the simpler cases of fractional crystallisation or distillation, by considering the commercial problem of the separation of benzene from its homologues, or benzene from carbon disulphide. Here, and in many other operations, the industry is calling for works managers who can apply the calculations and results of scientists to manufacturing conditions.

This need is not really met by introducing fragmentary accounts of the phase rule, &c., into the general pass degree courses. Physical chemistry, or branches of it, must be taken in separate courses. In the one especially designed for the works chemist arithmetic should predominate, and time will only be found for such parts of the subject, electrochemistry, thermochemistry, &c., as are of pressing importance, while others, although they have great theoretical importance and interest students, would have to be omitted from this course. The greater part of the time will be devoted to preparative work of the

kind mentioned, in which incidentally much experience will be gained in spectroscopy, calorimetry, &c. It thus seems possible in a relatively small institution to give technical graduates a sort of idea of the mental equipment that they will eventually require when they make good in the technical world.

Mr. H. L. HEATHCOTE (Coventry) wrote that in future training for the works must be *induced* by the needs of industrial processes, with their necessary limitations, rather than *forced* by the examination syllabus and academic atmosphere. He dwelt on the difficulties in assimilating or in turning to practical account the ideas of the scientific staff that obtained in practice on account of the inevitable constitution of the works and the limitations imposed by labour and material. Schemes for education and research should bear in mind these practical limitations and the science-man must be trained to overcome them. He must be a synthesist as well as an analyst.

Dr. P. E. SPIELMANN wrote that only a very exceptional man could combine in himself the knowledge and experience of both a highly skilled chemist and a fully qualified engineer. They ought, however, to aim at a training that would enable the chemist to criticise the engineer's drawings and the engineer to grasp the chemist's requirements.

Mr. FRANCIS H. CARR (Nottingham) also thought it rare to meet men endowed with both chemical and engineering sensitiveness, but more men with the combined aptitudes could be discovered and developed, and one great object of college training should be the discovery of the student's potentialities. Such complex chemical manufactures as have been developed here are due to men who have been trained in or had aptitude for both chemistry and engineering. The pure chemist is often timid in attacking practical problems outside the laboratory. He advocated the establishment in colleges of a department which could be conducted something like a factory carrying on side by side with lectures the production, say, of fine chemicals (that have hitherto been produced in Germany) on the scale of technical experiments. He submitted these proposals for serious consideration.

The subject being thrown open for general discussion,

Sir A. McDougall Duckham, K.C.B., supported from his personal practical experience Prof. Donnan's definition of the types of chemists and engineer-chemists required by industry. He went farther, and thought chemistry should be brought into every engineering course. He insisted on the importance of bringing the practical man and the practical work of the works into the colleges, and he thought also that students should enter works before college.

Prof. A. K. HUNTINGTON remarked that although a thing in a works was useless unless it could be done economically, it must be borne in mind that what does not pay to-day may very well pay under different conditions or with increased knowledge; the Haber process, which the Germans were carrying out on a huge scale, was a case in point. He suggested the use of the term "works engineer" to indicate the man trained to deal with works processes. A great difficulty at present in the training of technical students was the miserable equipment, especially in mathematics, received in the secondary school. He concluded with an appeal to the scientific man to enter the works and so, by acquiring really adequate data, ensure theory working out in practice.

Mr. A. P. M. FLEMING spoke of the importance of the engineer-chemist acquiring his experience in the works, and in this connection commented on the scheme for training industrial chemists at the Massachusetts Institute of Technology that Prof. Donnan had outlined, in which third-year selected men were put into, say, Portland cement works, or electrochemical or gas or alkali works, to enable them to pick up Mr. Cooper's "forgotten factor."

A further part of the plan was to organise at headquarters schemes of research in connection with each of the industries. He gave some interesting details of some of the post-graduate industrial research being carried out in America, and thought the universities here should develop similar schemes. Most important of all was to attract the best brains of the country into their profession.

Dr. W. ROSENHAIN emphasised the importance of breadth of view in the training of the technical man, which would enable him to face problems from many points of view. The simplification in conditions which was the essence of scientific research might be a drawback when dealing with practical problems, and hence the narrow expert would fail where the man of broad insight would succeed. But the man with scientific training is the man who is bound in the end to "make good," provided he is satisfactory material to begin with.

Dr. R. ROBERTSON thought the teaching of engineering to chemists essential, not only for its inherent value, but because it might be used by the professor as a touchstone to determine a student's true vocation—whether for pure research or applied science. He too agreed with the necessity for the student of contact with the reality of the works.

Mr. W. MACNAB spoke of the opportunity present circumstances afforded of putting into practice some of the excellent teaching they had heard propounded during the discussion. There was a sad lack of engineering chemists in the country. A hopeful sign was the breaking down of watertight compartments of knowledge.

Prof. E. G. COKER said there was often difficulty in placing young engineers with more brains than money in suitable positions, and he hoped for the general adoption of plans like that of Mr. Fleming. It must not be forgotten that many good chemists were not interested in engineering, and the reverse was also true, so that any educational scheme must be permissive. Courses of engineering for chemists should be specialised; much of the ordinary engineering could not possibly be of interest to chemists. He thought some of the American courses erred on the side of overloading, and preferred the English method of taking fewer subjects and doing them very thoroughly.

Lieut. H. C. GREENWOOD thought it lamentable that the process chemist should often have no share in the erection of the plant. The remedy may lie in better education, but early specialisation was generally a mistake, as students do not know what branch they will take up. While engineering in the way suggested by Prof. Donnan must be taught, more prominence should also be given to pure physical chemistry, which was becoming of increasing practical importance.

Mr. C. S. GARLAND spoke of the gain to chemists and to industry to be derived from enlarging their view by training in engineering and works experience. Sufficient inducement could be relied upon to bring the right men forward.

Dr. E. F. ARMSTRONG (Warrington), while expressing his agreement with Sir George Beilby and Prof. Donnan, did not think we had a shortage of plant chemists, who had been produced in goodly numbers by the universities. Moreover, after all, what chemical industry chiefly wanted was *chemists* first and then engineering chemists to tell the engineer what was wanted. While the works knows all about costs and management, it does not know, or is too busy to keep in touch with, modern developments in chemistry. To give an example: a man specially expert in the phase rule or colloidal chemistry put into a works might revolutionise many an existing process. Such men must be produced, and to do so not only must the university enter the works, but the manufacturer must enter the university, advise it, and support it. He did not altogether believe in the deficiencies of British chemical industry. The three great achievements in industrial chemistry in the last twenty years were artificial silk, fat-

hardening, and synthetic ammonia. The last did not appeal to us (before the war) because we had plenty of ammonia, but the first was an English achievement, discovered by an Englishman, Mr. Cross, and the second was largely worked out in Great Britain.

Mr. W. GATHORNE YOUNG (Doncaster) thought the meeting would be an epoch marking one and that we would proceed along the lines marked out by Prof. Donnan. After the first three years of training, only those students should take a course in chemical engineering who showed an aptitude for it. The course should include systematic visits, with demonstrations, to chemical works and vacation work at such factories. Manufacturers would co-operate if approached in the right spirit. He did not believe manufacturing processes could be taught by operating miniature plant in the laboratory. If some of our best brains have gone into other professions during the past thirty years, it is because of the miserable return that has been offered to chemists.

Mr. T. G. ELLIOTT agreed with those speakers who had laid stress on our general want of secondary education. He thought Prof. Donnan's scheme rather academic, and dwelt on the value of the university to a district when it specialised in the work of the district, such as had been done by Sheffield University, for example.

MODIFICATION OF THE PRATT METHOD FOR THE DETERMINATION OF CITRIC ACID.

By J. J. WILLAMAN.

In working with Pratt's method ("Determination of Citric Acid," *Circular* 88, 1912, U.S. Dept. Agric., Bur. of Chem.) for the determination of citric acid, considerable difficulty was encountered in getting duplicate determinations to agree. This difficulty was mentioned in the 1912 report of the Association of Official Agricultural Chemists, but no suggestions were made for remedying it ("Proceedings of the Twenty-ninth Annual Convention of the Association of Official Agricultural Chemists," 1912, *Bull.* 162, 60, U.S. Dept. Agric., Bur. of Chem.). It is believed that the modifications described herein will give very satisfactory results.

Discussion of Process.

The primary operations in this method are the fractional oxidation of the citric acid to acetone by means of potassium permanganate, the removal of the acetone as fast as formed by distillation, the formation of an insoluble mercury-acetone complex by boiling with mercuric sulphate, and the weighing of this precipitate. A thorough study has been made of each step of the process, in the attempt to discover all the influencing factors and the combination of procedures that would give the most satisfactory results. A discussion of the various investigations follows.

1. *Fractional Oxidation.*—The process is purely empirical, the results varying with each change of conditions. The potassium permanganate attacks any organic substance that may be present along with the citric acid, distributing itself among them according to the ease with which each is oxidised. Among the substances likely to be present in working with plant products are other acids brought down by the barium acetate, and sugars and colouring matter occluded by the barium precipitate. These cannot be washed out completely, hence are always present in greater or less amount, and capable of consuming permanganate. Acetone itself, the desired end-product of the oxidation of the citric acid, can, of course, be further oxidised; hence the necessity of removing it as fast as formed. It was found that the more dilute solution of citric acid is, the less the acetone obtained. This is undoubtedly due to the fact that if only a small amount of citric acid is present at the point of contact

between the drop of permanganate and the boiling liquid, the oxidation will proceed beyond the acetone stage before the acetone can escape, and before the drop of permanganate is consumed. Several factors, then, would tend to give larger yields of acetone, viz., (1) more concentrated solution of citric acid, (2) less concentrated solution of permanganate, (3) the presence of substances other than citric acid to partially consume the permanganate, (4) rapid boiling and slow addition of permanganate.

In Table I. are presented the results of a few of the experiments which were made to determine the effect of various changes of conditions on the yield of acetone. The several groups of determinations illustrate the four points enumerated above.

TABLE I.—Effect of various Changes of Conditions of Oxidation on the Yield of Acetone.

Factor under observation.	Citric acid present. Mgrm.	Vol. soln. start. Cc.	Strength of KMnO ₄ soln. per litre.	Citric acid recovered.	
				Mgrms.	Per cent.
Volume of solution of citric acid at start	(25 25 25)	(400 200 100)	(0.50 0.50 0.50)	(17.7 18.9 21.9)	(70.8 76.0 87.6)
Concentration of citric acid	(25 50 150)	(400 400 400)	(0.35 0.35 0.35)	(18.6 85.3 133.7)	(74.4 85.3 89.1)
Strength of KMnO ₄ solution	(50 50 50 50)	(100 100 400 400)	(0.20 0.50 0.35 0.70)	(46.9 45.2 43.8 42.0)	(93.8 90.4 87.6 84.0)
Rate of oxidation of citric acid—					
(11 mins.)	50	400	0.70	42.0	84.0
(16 mins.)	50	400	0.70	44.6	89.2
Presence of substances other than citric acid (a) ..	(50 75 50)	(100 100 100)	(0.50 (b) 0.50 (b) 0.20 (c))	(45.4 75.2 48.9)	(90.8 100.2 97.8)

(a) Blank determinations were made with these substances, and no mercury precipitate was obtained.

(b) 50 mgrms. tartaric acid added.

(c) 10 mgrms. sucrose added.

It is evident that if constant results are to be obtained a certain set of conditions must be adopted and then rigidly adhered to. This has been done in the proposed modified procedure. A volume of citric acid solution of 100 cc. at the beginning of the operation was chosen as the most convenient; ordinarily with 100 mgrms. citric acid present and no other oxidisable material, and the permanganate solution of 0.5 gm. per litre dropping in at the rate of 120 to 150 drops per minute, the reaction will be complete with a residual volume of 15 to 25 cc. in the flask. Thus the rate of distillation must be a little faster than the rate of flow of the permanganate. The volume of solution and a slightly increased rate of permanganate flow are the only items changed from Pratt's original specifications. Although the presence of substances other than citric acid does tend toward slightly higher results the effect has been found to be inconsiderable.

2. *The Concentration of Denigès's Solution*, in which the acetone distillate is boiled, has a very marked influence on the amount of mercury-acetone precipitate obtained; the stronger the solution the less the precipitate obtained. This is shown by the data in Table II., and may be due either to increased solubility of the compound or a change in its composition. Whatever the cause it can be avoided by always having the same concentration of mercuric sulphate. Pratt's directions call for 30 to 40 cc. of Denigès's solution in the distillate, but do not specify the volume of that distillate. Since the smaller the amount of oxidisable material the less is the time required for the operation, the smaller is the distillate, and

the more concentrated is the mercuric sulphate. The writer has adopted therefore a concentration of 15 cc. of Denigès's solution for each 100 cc. of distillate. The reaction is then proportional with all amounts of citric acid, at least those from 25 to 150 mgrms. Great accuracy in measuring the distillate is not required; a 700 or 800 cc. Erlenmeyer marked at 300, 400, and 500 cc. does very well.

TABLE II.—The Effect of the Concentration of Denigès's Solution on the Yield of the Acetone-mercury Compound. 50 mgrms. Citric Acid taken.

Volume of distillate containing 40 cc. Denigès's solution (cc.).	Recovery of citric acid (per cent.).
200	96.4
250	96.8
300	99.3
350	102.0
400	100.3
500	100.7

3. Amount of the Mercury-acetone Precipitate Formed.—

This was determined by Pratt by weighing on a Gooch. This has been found less easy and trustworthy than the process of determining the mercury in the precipitate by titration. As the precipitate has a tendency to adhere to the sides of the Erlenmeyer flask in which it is formed it is difficult to remove it completely to a Gooch. It is, however, readily dissolved by hot 5 per cent hydrochloric acid. The resultant mercuric chloride may be titrated against standard potassium iodide solution according to Personne's method (*Comptes Rendus*, lvi., 63; see also Sutton's "Volumetric Analysis," 10th edition, 1911, p. 264). This procedure was used in all the present experiments, and proved to be rapid and accurate.

4. *The Flow of Permanganate* into the oxidation flask in the writer's apparatus is controlled by a screw pinch-cock on a piece of soft rubber tubing, which replaces the glass dropping funnel in Pratt's apparatus. One end of the rubber tubing is connected to a bent glass tube passing through the stopper of the oxidation flask, and ending in a fine nozzle; the other end of the tubing connects with a 2 litre supply reservoir of permanganate. This arrangement gives better control of the flow of permanganate than the glass-stoppered dropping funnel.

5. *Oxidation Flask*.—A 200 cc. Kjeldahl flask with all but 3 cm. of the neck removed is very satisfactory. A 200 cc. side-arm distilling flask is equally good.

6. *Removing of the Citric Acid* from a plant juice with barium acetate. The writer has adopted a medium of 30 per cent alcohol instead of 50 per cent. It throws out all the citric acid, and only a little of the other acids, as pointed out by Jørgensen ("Über die Bestimmung einiger der in den Pflanzen Vorkommenden Säuren," *Zeit. Nahr. Genussm.*, 1907, xiii., 241). The precipitate is also more granular in this case, and thus more easily filtered and washed.

7. *Quantitative Relation*.—In order to determine the quantitative relation between the citric acid and the potassium iodide used to titrate the mercury of the final product, a series of analyses was made with varying amounts of pure citric acid, using the exact procedure as given below. The potassium iodide solution used contained 26.70 grms. KI per litre. The results are given in Table III. In order to compare the accuracy of these figures with those obtained by Pratt in ascertaining the factor to be used with his gravimetric method, an excerpt is given of his table (the last column was computed by the writer).

According to this procedure, then, 1.0 cc. of a solution of potassium iodide containing 26.70 grms. of the salt per litre is equivalent to 1.906 mgrms. citric acid. For convenience, a solution of potassium iodide of 28.0218 has been adopted, 1 cc. of which is equivalent to 2.0 mgrms. citric acid.

TABLE III.—Showing the Determination of the Factor for Potassium Iodide, in Comparison with the Factor in Pratt's Gravimetric Method.

Present Method.

Grm. citric acid.	KI solution.	KI solution per 1 gm. citric acid.	Recovery using value of 0.000906.
	Cc.	Cc.	Per cent
0.025	12.90	516	98.3
0.025	12.90	516	98.3
0.025	13.05	522	99.5
0.050	26.40	528	100.6
0.050	26.90	538	102.5
0.100	52.80	528	100.6
0.100	52.00	520	99.1
0.150	78.80	525	100.8
0.150	79.40	529	100.9

Average 524.7
or 1 cc. = 0.001906.

Pratt's Method.

Grm. citric acid used.	Weight of precipitate.	Calculated factor.	Recovery using factor 0.220. Per cent.
0.020	0.104	0.187	114.4
0.040	0.234	0.208	105.1
0.052	0.227	0.224	96.0
0.080	0.343	0.231	94.3
0.097	0.453	0.214	102.7
0.104	0.430	0.240	91.0
0.104	0.451	0.229	95.4
0.104	0.415	0.232	94.1
0.104	0.442	0.234	93.5
0.107	0.510	0.210	104.9
0.128	0.559	0.229	96.1
0.128	0.556	0.230	95.6
0.146	0.679	0.215	102.3
0.246	1.181	0.208	105.6
0.491	2.364	0.208	106.0

Average 0.220

The Modified Method in Detail.

The following solutions are required:—

1. Hydrochloric acid, 5 per cent (approximately).
2. Sodium hydroxide, 10 per cent.
3. Phosphoric acid, 6 per cent.
4. Denigès's solution made as follows:—Add about 500 cc. of water to 50 grms. of mercuric oxide; then add 200 cc. of concentrated sulphuric acid with constant stirring; make up to a litre, heat on a steam-bath an hour or two, and filter till clear.
5. Potassium iodide; contains 28.0218 grms. pure KI per litre. One cc. of this is equivalent to 2 mgrms. citric acid under the conditions of the experiment.
6. Mercuric chloride; contains 10.8038 grms. HgCl_2 and 25 grms. NaCl (to assist in solution) per litre. It is equivalent to the potassium iodide solution volume for volume. It is best made up by weighing out a slight excess of the salt, then standardising against the potassium iodide solution, and diluting to the proper strength.
7. Potassium permanganate, 0.5 gm. per litre.
8. Barium acetate, 10 per cent, in 30 per cent alcohol by volume.

The complete method of analysis follows. The directions are the same as given by Pratt, except where the present modifications enter in.

Throw out the pectins by adding twice the volume of 50 per cent alcohol. When the precipitate has settled, filter through paper on a Büchner funnel, and wash twice with 65 per cent alcohol, sucking the gelatinous precipitate as dry as possible. Dilute the filtrate with water to give approximately a 30 per cent alcohol content by volume, and add slowly 5 cc. of the barium acetate solution. When the barium citrate has settled to the bottom, filter

through asbestos in a Gooch, wash once with 30 per cent alcohol, and dry in a water-oven. The barium citrate is next dissolved with hot 6 per cent phosphoric acid solution, using three portions of 20 cc. each, and followed by hot water. The filtrate and washings should be about 100 cc. They are transferred to the oxidation flask, and the latter connected with a spiral condenser and with the device for adding potassium permanganate. To prevent bumping, introduce into the flask a piece of glass tubing sealed at the upper end and long enough to remain upright. Sometimes a few glass beads are also necessary. The adapter of the condenser dips into 40 cc. of Denigès's solution contained in a 500 cc. Erlenmeyer flask. Heat the citrate solution over a naked flame, then allow the permanganate to drop into the briskly boiling solution at the rate of 20 to 25 drops in ten seconds. When a deep pink colour has persisted for a couple of minutes the reaction is complete. If the volume of liquid in the flask becomes too small, excessive portions of 20 cc. of water may be added, care being taken to shut off the flow of permanganate a few moments before the distillation is stopped, and the system is opened. The distillate is made up to 300 cc., put under a reflux condenser, and boiled gently for forty-five minutes. If the distillate is over 300 cc. more Denigès's solution should be added at the rate of 15 cc. for each 100 cc. of distillate in excess of 300 cc.

The precipitate is filtered hot through paper, washed by decantation twice with hot water, then the filter paper washed thoroughly. The precipitate in the Erlenmeyer is dissolved in two or three small portions of 5 per cent HCl by heating, each portion being poured through the filter containing the rest of the precipitate, and collected in a 100 cc. flask. The acid solution is returned through the filter till all precipitate is dissolved. After thoroughly washing the filter and flask with hot water the filtrate is cooled, very nearly neutralised with 10 per cent sodium hydroxide, and made up to 100 cc. The mercury can now be titrated by either one of the two following methods.

—(a) The whole or an aliquot of the mercury solution can be poured into an excess of the potassium iodide solution, and the excess potassium iodide titrated back with the standard mercuric chloride solution. The amount of potassium iodide solution necessary for the whole sample can then be calculated, together with the citric acid equivalent. (b) The mercuric chloride solution under examination can be placed in a burette, and titrated directly against, say, 10 or 15 cc. of the standard potassium iodide, and the amount of citric acid in the whole sample computed. For amounts of citric acid of 100 mgrms. or over, (b) is the preferable procedure. If (a) is used the aliquot used should not be less than one-fourth.

Malic, tartaric (except quantities of 0.5 gm. or over), oxalic, and aconitic acids do not interfere with this determination. The presence of much sugar, or other substances capable of reducing permanganate, tends to give slightly high results, but the difference is inconsiderable.

TABLE IV.—The Analysis of certain Plant Products for Citric Acid.

The Author with Modified Method.

Substance analysed.	Citric acid (per cent).	
	0.599	0.586
Sorghum syrup	0.599	0.586
Lemon juice, titrating 6.64 per cent citric acid	6.69	6.64
Grape fruit juice, titrating 0.90 per cent citric acid	0.976	0.993

A.O.A.C. Collaborators with Pratt's Method, using Orange Juice Titrating 0.83 per cent Citric Acid.

Collaborator.	Citric acid (per cent).					
	0.79	0.89	0.79	0.76	0.84	—
J. M. J. ..	0.79	0.89	0.79	0.76	0.84	—
P. A. Y. ..	0.824	0.836	0.787	0.840	—	—
P. B. D. ..	0.72	0.73	0.63	0.72	0.69	—
H. C. G. ..	0.81	0.80	0.73	0.87	0.80	0.84

In order to show the accuracy of duplicate determinations by the modified method several products were analysed for citric acid. The results are shown in Table IV. For the sake of comparison the table of results given in the 1912 Report of the A.O.A.C. is also reproduced.

These results seem to warrant the conclusion that the modified method, if followed rigidly, will give much more satisfactory results than the original one. It is hoped that other workers will give the proposed method a trial, as a trustworthy method for determining citric acid in plant products is needed.—*Journal of the American Chemical Society*, xxxviii., No. 10.

ON THE PREPARATION AND IONISATION OF THE DIALKYLPHOSPHORIC AND BENZENEDISULPHONIC ACIDS.*

By W. A. DRUSHEL and A. R. FELTY.

(Concluded from p. 163).

Conductivity and Hydrolysis Measurements.

THE apparatus used in this work was the usual conductivity apparatus—a Wheatstone bridge previously calibrated, an ordinary Ostwald cell whose constant was determined with N/50 potassium chloride, an alternating induction coil with high frequency vibrator and telephone receiver, a standard plug resistance box, a pair of carefully calibrated 10 cc. pipettes, and a thermostat kept at 25°.

(a) *Ionisation of Dialkylphosphoric Acids.*—The molecular conductivities of the sodium salts of the dialkylphosphoric acids were first determined at different dilutions, starting with N/8 solutions. From these measurements the values of μ_{∞} were determined by the method of graphic extrapolation described in Ostwald-Luther ("Physiko-Chemische Messungen," 414, 2nd ed.). To obtain the values of μ_{∞} for the acids the corrected values of the sodium salts were diminished by the ionic conductivity of the Na ion (51) and increased by that of the H ion (347). The molecular conductivity of the dimethylphosphoric and dipropylphosphoric acids were determined in this way. In attempting to dehydrate the sodium diethylphosphate slight decomposition occurred, giving a value for μ_{∞} abnormally high. This value was therefore rejected, and the value of μ_{∞} for the corresponding acid determined by Van Hove was used.

(NOTE.—Van Hove, *Bull. Acad. Roy. Belg.*, 1909, p. 282, determined by the conductivity method the dissociation of diethylphosphoric acid, but no previous work is reported on the dissociation of its homologues. His average value for k was 10.03×10^{-2}).

The molecular conductivities of the three homologous dialkylphosphoric acids were measured for dilutions ranging from N/8 to N/1024. The value of μ_{∞} for dipropylphosphoric acid obtained by the graphic method was verified by direct measurement at high dilution. The mean of the two values (389.5) was used in the calculations. From the values obtained by direct measurement and calculation the degrees of ionisation of the acids expressed in per cent were found, also the affinity constants of the acids were calculated from the formula of Ostwald, $k = a^2/(1-a)v$. The values found for the dialkylphosphoric acids are recorded in Table I.

(b) *Ionisation of the Isomeric Benzenedisulphonic Acids.*—The benzenedisulphonic acids represented by the general formula $C_6H_4(SO_3H)_2$ are dibasic, and are dissociated similarly to sulphuric acid at different dilutions into the ions H^+ and $C_6H_4(SO_3H)SO_3^-$, and finally into H^+ , H^+ , and $C_6H_4(SO_3)_2^{2-}$; that is, at moderate concentration one H ion splits off, and on dilution the second H ion is formed.

TABLE I.

A. Degrees of Ionisation of Dialkylphosphoric Acids. 25°.

Dilution. v.	Me_2HPC_4 .		Et_2HPO_4 .		Pr_2HPO_4 .	
	μv .	Per cent dissociated.	μv .	Per cent dissociated.	μv .	Per cent dissociated.
8	262.6	69.3	236.8	62.2	227.2	58.25
16	292.3	77.1	274.4	72.1	266.7	68.4
32	317.0	83.7	304.6	80.0	296.9	76.1
64	335.0	88.4	328.5	86.26	325.9	83.56
128	348.0	91.85	344.7	90.51	342.0	87.68
256	356.0	93.95	354.9	93.20	354.2	88.70
512	362.7	95.7	362.5	95.20	366.1	93.86
1024	367.8	97.05	365.7	96.03	379.9	95.20

μ_{∞} 379.0 (Graphic) μ_{∞} 379.0 (Van Hove) μ_{∞} 389.5 (388—graphic) (391—direct)

B. Affinity Constants of the Dialkylphosphoric Acids. 25°.

Dilution.	Me_2HPO_4 . k .	Et_2HPO_4 . k .	Pr_2HPO_4 . k .
8	19.5×10^{-2}	12.8×10^{-2}	10.1×10^{-2}
16	17.0 "	11.6 "	9.2 "
32	13.1 "	10 "	8 "

Considerable work has been done on the sulphonic acids of benzene derivatives, but conductivity measurements of the simple unsubstituted benzenedisulphonic acids have apparently not been previously reported. Ebersbach and Ostwald (*Zeit. Phys. Chem.*, 1893, xi., 617) determined the conductivities of ortho- and meta-toluidinesulphonic acids, $C_6H_2NH_2CH_3(SO_3H)_2$, in order to ascertain the effect of the different positions of the methyl group on the dissociation of the acids. Armstrong and Worley (*loc. cit.*) studied a number of sulphonic derivatives, but their work on the simple benzenedisulphonic acids was confined to the use of three isomeric acids as catalytic agents in the hydrolysis of cane sugar in order to determine their relative strengths. They found the meta-acid slightly stronger than the para-acid, and both very much stronger than the ortho-acid. Our results—obtained both by the conductivity method and the hydrolysis method—are only partially in agreement with the results of Armstrong and Worley. Both methods of measurement gave concordant results, and show the para-acid to be a little stronger than the meta acid and both very much stronger than the ortho acid. Our results are really in better agreement with Armstrong and Worley's structure theory for the explanation of the catalytic action of the three isomeric benzenedisulphonic acids than their results, although these acids, as shown by our conductivity measurements, require no special structure theory to explain their catalytic activity. The general ionisation theory amply covers the case of the three isomeric benzenedisulphonic acids. The results of our conductivity measurements are given in Table II.

TABLE II.—Conductivities and Degrees of Dissociation of the Isomeric Benzenedisulphonic Acids. 25°.

Dilution. v.	Ortho-acid.		Meta-acid.		Para-acid.	
	μv .	Per cent dissociated.	μv .	Per cent dissociated.	μv .	Per cent dissociated.
8	317.2	83.09	339.2	88.64	343.3	89.47
16	329.4	86.28	351.5	91.63	353.8	92.21
32	341.3	89.39	359.3	93.66	361.6	94.24
64	351.9	92.17	367.3	95.75	370.5	96.56
128	361.1	94.59	374.2	97.52	375.2	97.78
256	367.5	96.79	380.1	99.09	380.1	99.06
512	374.7	98.06	383.6	100.00	383.1	99.84
1024	377.5	98.90	—	—	383.7	100.00
2048	381.7	100.00	—	—	—	—
2048	381.6	100.00	By single dilution.			

(c) *Catalytic Action of the Isomeric Benzenedisulphonic Acids in the Hydrolysis of Ethyl Acetate.*—The ionisa-

* From the *American Journal of Science*, xliii., p. 57.

tion of these acids as determined by the conductivity method was confirmed by using them in decinormal concentration in the hydrolysis of ethyl acetate at 25°. In order to determine positively the relative strength of the meta- and para-acids, duplicate measurements were made for these two acids. For the purpose of comparison hydrochloric acid in decinormal strength was also used for the hydrolysis of ethyl acetate. Titrations were made in the usual way, and the constants were calculated from the usual titration formula for reactions of the first order. The results obtained with these acids are given in Table III.

TABLE III. — Isomeric Benzenedisulphonic Acids as Catalytic Agents in the Hydrolysis of Ethyl Acetate. Acids Used in Decinormal Solutions at 25°.

HCl. 10s K.	Ortho-acid. 10s K.	Meta-acid. 10s K.	Para-acid. 10s K.
64.4	67.2	(76.0)	73.8
65.0	65.2	72.4	74.8
63.3	—	72.2	73.7
65.4	65.1	72.0	75.6
64.0	64.0	73.9	75.1
63.6	—	72.4	73.1
62.2	64.6	75.5	(77.3)
64.0	65.2	73.0	74.35
		72.9 (a)	74.50 (a)

(a) Duplicate.

Summary.

1. The lower homologous dialkylphosphoric acids may be prepared by the action of barium hydroxide upon the trialkyl esters and the decomposition of the barium salts with sulphuric acid.

2. The degree of dissociation of the dialkylphosphoric acids decreases regularly with the increase in the molecular weight of the alkyl groups.

3. The isomeric benzenedisulphonic acids may be prepared, each entirely free from its isomeric forms, by a proper choice of methods. In this connection the xanthate method of converting amidobenzenesulphonic acids into the corresponding benzenedisulphonic acids gives good results under favourable conditions.

4. The catalytic activity of the isomeric benzenedisulphonic acids is in the order ortho-, meta-, and para-. The relative catalytic activity of the three acids requires no special explanation based upon a structure theory, but is in agreement with the general ionisation theory.

THEORY OF COLLOIDS.

By JOHN ARTHUR WILSON.

THE object of the present paper is the promulgation of further reasoning in favour of the "complex" theory of colloid formation, and the elucidation of the very interesting and important conclusions which follow. The fundamental assumption of this theory is that the colloidal state in sols owes its stability to the formation of a complex between the particles of the disperse phase and certain substances present or formed in the dispersion medium during the preparation of the colloid. The sols of the noble metals have been cited as an argument against this theory, but Beans and Eastlack (*Journ. Am. Chem. Soc.*, 1915, xxxvii., 2667) have shown that the presence of chloride, bromide, iodide, or hydroxide ions in concentrations from 0.00005 N to 0.005 N has a marked stabilising effect on gold sols, and that the colloid particles become negatively charged. In concluding, these authors consider that the electrical synthesis of colloids consists of a thermo-mechanical dispersion of the metal, followed by the formation of a colloidal complex between the dispersed metal and certain ions present in the medium.

The assumption of the formation of such a complex between any colloid particles and electrolytes present in the dispersion medium is not unreasonable. Carbon is a typical adsorbing agent and happily one the stability of whose compounds has been extensively investigated. The data leading to the formulation of Baeyer's S rain Theory indicates that the four valencies of the carbon atom are directed toward the vertices of a regular tetrahedron of which the carbon atom is the centre. This being true, any atom within a given particle of carbon will attract and be attracted by the atoms immediately surrounding it, but one at the surface is attracted only towards atoms of the particle, and consequently has one or more of its valencies directed away from the particle, and therefore unsatisfied. In a lump of carbon this free or residual valency might be relatively insignificant but would increase to huge proportions as the carbon became more and more highly dispersed. It is probable that every substance possesses a certain amount of residual valency at its surface, which tends to cause it to combine with substances approaching its surface. As in chemical combination in general, such combination is probably selective. Indeed, Beans and Eastlack (*loc. cit.*) have shown that the presence of fluoride ions does not stabilise gold sols, while Lenher (*Journ. Am. Chem. Soc.*, 1903, xxv., 1136) has shown that gold fluoride is incapable of existence, not only in the presence of water, but under ordinary laboratory conditions.

Apparently the colloid particle takes its electrical charge from the ions with which it combines, or, in some cases, acquires a charge by ionising itself. Such a charge seems to be necessary to the stability of the colloid state in sols, which is explained to some extent by the fact that particles with like charges tend to repel each other, thus preventing coalescence.

Associated with any charged particle there will be a number of ions of opposite charge, which cannot be separated from the surface of the particle, excepting by very small distances, or by being replaced by other ions of the same sign, which means that the distribution of ions in the layer of solution surrounding the particle will be different from that in the bulk of the dispersion medium, a condition to which Donnan's work on membrane equilibria can be applied (*Zeit. Electroch.*, 1911, xvii., 572). Donnan considers an aqueous solution of a salt, NaR, such as congo red, in contact with a membrane which is impermeable to the anion R' and the nonionised salt, but will allow Na+ or any other ion to pass freely through it. On the other side is an aqueous solution of sodium chloride, which will diffuse from its Solution II. into the Solution I. of NaR. When equilibrium is established, if a small virtual change is made reversibly at constant temperature and volume, the free energy will remain unchanged; i.e., no work will be done. The change here considered is the transfer of δn moles of Na+ and Cl' from II. to I. The work which equals zero is—

$$\delta n RT \log \frac{[\text{Na}^+]_{\text{II}}}{[\text{Na}^+]_{\text{I}}} + \delta n RT \log \frac{[\text{Cl}^-]_{\text{II}}}{[\text{Cl}^-]_{\text{I}}} = 0,$$

or—

$$[\text{Na}^+]_{\text{II}} \times [\text{Cl}^-]_{\text{II}} = [\text{Na}^+]_{\text{I}} \times [\text{Cl}^-]_{\text{I}}.$$

By a continuation of this reasoning it can be shown that whatever diffusible binary electrolytes be added to Solution II., when equilibrium is established, the products of concentrations of any pair of diffusible and oppositely-charged ions will be equal in the two solutions.

If a substance is dispersed to the colloid state in a solution of the electrolyte MN and combines with a portion of M+ (not necessarily in equivalent quantity from a chemical standpoint), then at the surface of the colloid particles there will be a certain concentration of N' bound by electrochemical attractions to the colloid. This surface layer of solution will also contain M+ and N-, and will thus bear the same relation to the bulk of solution as did Solution I. to Solution II. in Donnan's work just quoted, and consequently the product $[\text{M}^+] \times [\text{N}^-]$ will be equal in the

surface layer and the bulk of solution, and since the concentrations of M^+ and N^- are unequal in the surface layer and equal in the bulk of solution, the total concentration of ions will be greater in the former than in the latter.

In the bulk of solution let x = concentration of positive or negative ions.

In the surface layer surrounding particle let y = concentration of ions of same sign as charge on the colloid particle.

z = concentration of ions bound to the colloid by electrochemical attractions.

Therefore $y+z$ = concentration of ions of opposite sign to that on the colloid particle.

Let e = excess of concentration of diffusible ions of the surface layer over that of the bulk of solution.

In order to keep the reasoning as simple as possible only binary electrolytes will be considered, although it will be obvious that the reasoning can be extended to include ions of any valency. From the law of "equality of products" just discussed—

$$x^2 = y(y+z)$$

and since—

$$2x+e = 2y+z$$

$$z = \sqrt{4ex + e^2}.$$

If unit quantity of colloid and unit volume are considered, z represents the quantity of electrolyte combined with the colloid. But the generally accepted empirical formula for adsorption (using the same system of notation is—

$$z = kx^{1/\beta}$$

where β represents a constant, usually about 2, so that generally—

$$z = k \sqrt{x}.$$

The similarity of the equations is striking, and in certain cases, and within limits, they would give similar curves, but they are not identical, and here it should be noted that the latter formula is at best only empirical, while the former follows from well-founded assumptions.

The different distribution of ions in the surface layer and bulk of solution will result in a difference of potential, the formula for which is given by Donnan (*loc. cit.*) as follows:—

$$E = \frac{RT}{F} \log \frac{1}{\lambda}.$$

Or, in the notation adopted in this paper,—

$$E = \frac{RT}{F} \log \frac{x}{y} = \frac{RT}{F} \log \frac{2x}{-z + \sqrt{4x^2 + z^2}}.$$

But z has a limiting maximum value, since the amount of electrolyte which can combine with a colloid of definite degree of dispersion is limited by the amount of residual valency at the surface, or, in the case of an ionising colloid, the portion ionised cannot exceed the whole. Hence,—

$$\lim_{x \rightarrow \infty} E = \frac{RT}{F} \log \frac{2x}{\sqrt{4x^2}} = 0,$$

proving that the difference of potential existing between the surface layer surrounding the colloid particle and the bulk of solution will diminish as the concentration of electrolyte is increased, after the combination of colloid and electrolyte has reached or neared its maximum. When this difference of potential has become sufficiently small a condition is established which is favourable to the coalescence of the particles. Assuming that a given potential difference is required for the maintenance of the colloid state in sols, the amount of electrolyte required for precipitation of the colloid will depend upon the maximum value for z . In the case of suspensoids this is probably very small, while for many emulsoids it is known to be comparatively high.

Where a charged particle combines directly with an ion of opposite sign, precipitation must follow. The cause of the co-precipitation of oppositely charged colloids is equally obvious, but it might be well to point out in passing that the rate of this precipitation might be controlled by suitable regulation of the concentration of electrolytes in the dispersion medium. Similar lines of reasoning explaining the swelling and contracting action of electrolytes upon colloid jellies have been worked out by H. R. Procter and the author, and appear elsewhere (*Journ. Chem. Soc.*, 1916, cix., 307; *Journ. Am. Leather Chem. Assoc.*, 1916, xi., 8). Whatever herein expressed may seem opposed to the generally accepted views on colloids can be tested as the formulæ derived are quantitative in character. The author expresses the hope that they may lead a step nearer to the goal of colloid chemists.—*Journal of the American Chemical Society*, xxxviii., No. 10

EXPERIMENTS UPON STARCH AS SUBSTRATE FOR ENZYME ACTION.*

By H. C. SHERMAN and J. C. BAKER.

THE forms in which starch has been used as substrate for enzyme action may be grouped as:—1. Natural starch dispersed in water under different conditions of time, temperature, and pressure but without "chemical" treatment; 2. starch which has been subjected to the action of acid (Lintner) (*Journ. Prakt. Chem.*, 1886, [2], xxxiv., 378; see also Ford, *Journ. Soc. Chem. Ind.*, 1904, xxiii., 414) or to other chemical treatment (Wolff and Fernbach) (*Comptes Rendus*, 1905, cxl., 1403; 1906, cxliii., 363, 380) to render it "soluble"; (3) fractions of the starch substance which have been separated from the remainder by sedimentation (Tanret, *Bull. Soc. Chim.*, 1915, [4], xvii., 83), or precipitation (Maquenne and Roux, *Comptes Rendus*, 1905, cxl., 1303; *Ann. Chim., Phys.*, 1906, [8], ix., 179), Fernbach (*Proc. 8th Intern. Congr. Appl. Chem.*, 1912, xiii., 131), Malfitano and Moschkoff, *Comptes Rendus*, 1910, cl., 710; 1910, cli., 817), Gruzewska *Ibid.*, 1908, cxlvi., 540; 1911, clii., 785).

In order to ensure uniformity of substrate in successive experiments and to avoid difficulties due to imperfect solution or unequal dispersion on the one hand, or on the other hand the use of substrate representing only a part of the original starch and perhaps contaminated by the reagent or solvent used in its preparation, the consensus of opinion of workers in this field has favoured the use of "soluble" starch, prepared by Lintner's method of simply soaking the starch grains in cold hydrochloric acid and subsequently removing the latter by washing with cold water. Such "soluble" starch has been used in nearly all the studies of amylases carried on in this laboratory and has always been found a satisfactory substrate except for certain peculiarities encountered in the case of purified malt amylase.

When soluble starch is acted upon by pancreatic amylase either in purified or commercial form under the conditions used for measuring the amylolytic activities of enzyme preparations, the weight of maltose produced is regularly about half of the weight of starch which disappears. In other words the purified pancreatic amylase having many times the power of commercial preparations shows nevertheless the same relation between amylolytic and saccharogenic powers (Sherman and Schlesinger, *Journ. Am. Chem. Soc.*, 1913, xxxv., 1784). Similarly in experiments upon the amylase of *Aspergillus oryzae*, the amylolytic and saccharogenic activities were found to increase in about the same proportion as the enzyme was concentrated by purification (Sherman and Tanburg, *Ibid.*, 1916, xxxviii., 1638). But when purified malt amylase prepara-

* From the *Journal of the American Chemical Society*, xxxviii., No. 9.

tions were compared with malt extracts no such constancy in the ratio of amylolytic and saccharogenic powers was found. In this case not only had the purification process altered the ratio of amylolytic and saccharogenic activities, but evidently also the generally accepted method for measuring amylolytic action (that of Wohlgemuth) yields misleading results when applied to purified malt amylase.

The present investigation had its origin in an attempt to prepare a substrate sufficiently homogeneous to yield reliable results when used as in the Wohlgemuth method, and developed from this into a study of the differing behaviour toward enzymes of the two chief constituents of starch. It was thought that the discrepancy noted in the measurements of amylolytic action of malt amylase might be due to an unequal susceptibility of the two main constituents of starch to the action of the enzyme, in which case an approximate separation of the substances might yield a more satisfactory substrate. At the same time it seemed very desirable that the material to be used as substrate in our experiments should not be subjected to treatment with strong reagents nor to solution and reprecipitation, which might involve danger of change in its behaviour toward enzymes.

(NOTE.—Meyer (Untersuchungen über die Stärkekörner) considered starch to be chiefly composed of two substances to which he gave the names α -amylose and β -amylose. Maquenne and Roux (*loc. cit.*) call about four-fifths of the starch substance "amylose" and about one fifth "amylpectin." Gruzewska (*Comptes Rendus*, cxlv., 540; clii., 785) by solution in alkali and precipitation with alcohol estimated the "amylpectin" to be 40 to 45 per cent of the starch. Samec (*Koll. Beihefte*, vi., 32) by a modification of Gruzewska's method found 56 per cent of "amylpectin" and only 44 per cent of "amylose," the latter being practically phosphorus-free while the former contained phosphorus as an essential constituent. Tanret (*Bull. Soc. Chim.*, [4], xvii., 83) by successive treatment of starches with hot water, sedimentation, and decantation, finds from 70 to 80 per cent of "amylpectin" or "amylphosphate" and 20 to 30 per cent of "amylose." For the material present in larger quantity the term α -amylose not only has priority but is much more appropriate than the term amylpectin. We have therefore given preference to Meyer's terminology in this paper, even though some of Meyer's views as to the chemical nature and relationships of the α - and β -amyloses may not be tenable).

Experiments were therefore made to test the feasibility of extracting the more soluble component (" β -amylose," "amylose") while leaving behind the less soluble (" α -amylose," "amylpectin") by carefully regulated treatment of purified potato starch with distilled water. By ultrafiltration or by simple sedimentation we did not obtain satisfactory separations, but by use of the centrifuge much better results were obtained.

Separation of "Soluble" and "Insoluble" Components of Starch by means of Centrifugal Force.

When thin starch paste is submitted to centrifugal force it is separated into a lighter, clearer, and more limpid layer containing the more soluble constituent (β -amylose of Meyer, amylose of Maquenne and Roux) and a heavier, opalescent, very viscous layer containing the less soluble component (α -amylose of Meyer, amylpectin of Maquenne and Roux, amylophosphate of Tanret). For the purpose of making such separations we have employed three different types of centrifuge, but in all of the experiments here described the Size 1, Type A, 8-tube centrifuge of the International Instrument Company has been used. In these experiments 50 cc. of the starch paste are placed in each of the eight tubes of the centrifuge and rotated for thirty minutes at about 2400 revolutions per minute ("relative force 1024 times gravity"). At the end of such treatment the liquid in each tube is found to have separated into two distinct layers, the heavier opalescent layer

usually occupying from one-third to four-fifths of the total volume.

It was thus found possible to carry out a series of experiments, heating the starch with water under different conditions, separating the two portions, observing their properties, and using them as substrates for the study of diastatic hydrolysis.

Experiments upon Commercial Potato Starch.—In the earlier of our experiments a good grade of commercial potato starch was used. The starch was handled in air-dry condition and allowance was made for the moisture it contained when weighing out portions for experiment. All statements of weight or concentration of starch refer, therefore, to the water-free substance. Only one of these earlier experiments will be described here.

In this case starch was gelatinised in 100 times its weight of water at 85°, and the temperature maintained by means of a thermostat while the liquid was stirred continuously. Portions of the liquid were withdrawn and centrifuged at intervals. The centrifugates were studied with reference to volume, viscosity, concentration, and behaviour under the action of pancreatic and malt amylases. In the enzyme experiments the time required for the digestion of starch to disappearance of blue iodine reaction, and to disappearance of red reaction with iodine, was observed, and the maltose which had been formed at the time of disappearance of blue iodine reaction was determined. The iodine tests were applied under the conditions prescribed by the Wohlgemuth method and the "disappearance of blue" was considered to be that point at which the colour obtained with iodine changed from red-violet (RV) to violet red (VR), the colours being always determined by comparison with the Milton-Bradley Standard Colour Chart as given in Mullikin's "Identification of Pure Organic Compounds." The data obtained are shown in Table I.

TABLE I.—Properties of Unfiltered Centrifugates from 1 per cent Potato Starch Pastes Prepared at 85°.

Time of heating (hours)	1	2	4	6	8
Volume of lower layer (per cent) ..	60	66	65	61	47
Volume of centrifugate (per cent) ..	40	34	35	39	53
Viscosity of centrifugate (a)	1'445	1'572	2'130	2'335	3'06
Concentration of starch in centrifugate (per cent) ..	0'384	0'444	0'572	0'716	0'816
Digestion with pancreatin—					
To disappearance of blue reaction (mins.)	10'0	11'5	14'5	18'5	20'0
To disappearance of red reaction (mins.)	20'0	24'0	32'0	42'0	46'0
Maltose at end of blue in percentage of starch (60'5)	48'5	46'2	48'8	44'7	
Digestion with malt amylase—					
To disappearance of blue reaction (mins.)	18'0	19'0	20'0	24'0	26'0
To disappearance of red reaction (mins.)	24'0	28'0	40'0	55'0	65'0
Maltose at end of blue in percentage of starch	83'2	81'2	75'0	69'2	68'0

(a) Viscosities are here expressed as time of flow or solution divided by time of flow of water, both at 30°, Oswald viscosimeters being used.

When starch pastes are separated by centrifugal force as above described, the lower (heavier) layer is found to consist largely of greatly swollen grains. The swelling of the grains increases with duration of heating in water and appears to be due to absorption of water by the "insoluble" constituent of the starch grain, the "soluble" constituent going into solution.

From the data given in Table I. for volumes of lower layers and centrifugates from pastes prepared by heating for five different lengths of time at each of three temperatures, it would appear that in this particular series of experiments the swelling of the grains and liberation of the soluble component was the chief effect of heating the starch in 100 times its weight of water up to about two hours at 85°, and that the chief result of further heating at 85° was dispersion (or hydration) of the insoluble component into forms (or derivatives) not removable from the centrifugate by the force here employed (about 1000 times gravity for thirty minutes). Microscopic examination showed that the upper layer did contain some swollen grains. In subsequent experiments these were removed by filtering through paper covered with a thin layer of absorbent cotton. Observations upon the iodine reactions and phosphorus content of the two layers obtained in this and several subsequent experiments also bear upon this phase of the problem. The results of the action of amylases upon the centrifugates obtained after different periods of heating in water at 85°, also throw light upon the nature of the starchy material contained in this layer, and upon the differing ratios of amylolytic to saccharogenic powers as between pancreatic and malt amylases.

Thus it will be seen from the data given in Table I. that the pancreatic amylase acted in much the same way upon the different substrates. The time required for the digestion of the material to a point where iodine no longer gave a blue or violet reaction ("disappearance of blue") was approximately proportional to the amount of starch material present, the time required for "disappearance of red" was approximately twice that for "disappearance of blue" in all cases, and the maltose found at the time when the blue reaction had just disappeared was always about half the weight of the original substrate, as had been found by previous workers in this laboratory in experiments in which the enzyme acted upon soluble starch prepared by the Lintner process. On the other hand, it is apparent that the malt amylase acted differently upon the substrates obtained after different lengths of heating. The time required for disappearance of the red reaction with iodine increased more than did the concentration of the substrate in the successive portions; and the relative yield of maltose at the time of disappearance of the blue reaction is greatest for the substrate first obtained and decreases progressively for the substrates prepared by longer heating.

All of the results are consistent and together they indicate plainly that the continued heating results in dispersion of more and more of the less soluble component of the starch (α -amylose, amylopectin) into the solution of the more soluble component (β -amylose, amylose). (There remains the possibility that by heating with water the less soluble component of the starch grain may be slowly changed into the more soluble— α -amylose into β -amylose as suggested by Meyer).

With pancreatic amylase the digestion of the two components proceeds proportionately, so that the ratio of apparent amylolytic and saccharogenic activity is not materially disturbed by the difference in nature of the substrate; but with malt the two components are hydrolysed quite differently, so that with increasing proportion of the less soluble component (α -amylose, amylopectin) in the substrate the ratio of times required for disappearance of the blue and red reactions and the ratio of amylolytic and saccharogenic action are both altered.

(To be continued).

PROCEEDINGS OF SOCIETIES.

SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS.

Ordinary Meeting, April 4, 1917.

Mr. GEORGE EMBREY, President, in the Chair.

Mr. Hubert Charles Siegfried de Whalley was elected a Member of the Society.

A certificate for election was read for the first time in favour of Capt. N. M. Comber, A.R.S.C., B.Sc. (Lond.).

The following papers were read:—

"Natural Occurrence in certain Fish Liver Oils of High Percentages of Hydrocarbons." By A. CHASTON CHAPMAN.

A sample of oil from certain species of sharks caught off the coast of Morocco has been found to contain 90 per cent of unsaponifiable matter, consisting almost entirely of a new unsaturated hydrocarbon to which the name *Spinacene* has been given, and which has the formula $C_{30}H_{50}$. The existence of such oils is discussed from the analytical point of view, and it is shown that there would appear to be two main classes of shark-liver oils—the one having a specific gravity of about 0.86, and containing a very high percentage (up to 90 per cent) of unsaponifiable matters, and the other having a specific gravity of 0.910 to 0.930, and consisting largely of glycerides with smaller proportions of unsaponifiable matters consisting largely of cholesterol. Since these oils have totally different chemical characters and could not be used for the same purposes, it is clear that the simple designation "shark liver oil" is insufficient, and that such oil will in future have to be sold strictly on the results of analysis.

"Note on the Inflammability of Petroleum Spirit at Low Temperatures." By J. H. COSTE.

Determinations of the flash-point of three brands of petroleum spirit (-11° C. to -30° C.) and of acetone (-9.5° C.) were made in a wide test-tube, liquid air being used for cooling the substances examined. A calibrated thermo-couple was used for the temperature measurements. The sample of Pratt's spirit solidified at -128° C. and the acetone at -95° C.

"Determination of Volatile Thinners in Oil Varnishes." By ARMAND DE WAELE and FREDERICK SMITH.

The authors criticise those methods in which volatile solvent is estimated by loss in weight after spontaneous evaporation, as being the resultant of true evaporation and oxygen absorption. The authors' method is given as follows:—

3 to 4 grms. of varnish are weighed into a 200 cc. silica carbon dioxide flask containing a piece of broken glass, 60 to 70 cc. of boiling water are added, and boiled over a small free flame until the vapour no longer smells of volatile solvent. The remaining water is poured off, cooling if necessary, and any included water in the residue removed by boiling off on a water-bath with successive small quantities of alcohol and acetone until free from cloudiness. The acetone vapour in the flask is then blown out, the flask cooled and weighed.

The authors claim that their method offers advantages over that of McIlhenny in permitting of the subsequent examination of the residue for gums, &c., whilst not introducing errors caused by solubility of solvent in water, solvent adhering to apparatus, &c.

Royal Institution.—A General Meeting of the members of the Royal Institution was held on the 2nd inst. Charles Hawksley, Esq., Vice-President, in the Chair. Mr. Murray Stewart was elected a member. A Resolution of Condolence with the relatives of the late Prof. Jean Gaston Darboux, an Honorary Member of the Royal Institution, was passed.

NOTICES OF BOOKS.

Failure of Brass. (2) *Effect of Corrosion on the Ductility and Strength of Brass*, by PAUL D. MERICA; (3) *Initial Stress produced by the "Burning in" of Manganese Bronze*, by PAUL D. MERICA and C. P. KARR. Washington: The Bureau of Standards.

THESE two papers contain reports of investigations which have been carried out in the study of the causes of the failure of brass castings. The results appear to show that the decrease of the ductility and strength of brass caused by corrosion under stress is due to the increased E.M.F. At the bottom of the small furrows produced by corrosion the increased stress gives rise to a galvanic couple, so that the bottom is further corroded, and finally a crack is caused. The stresses introduced into a casting by burning in or welding a constrained area are discussed, and suggestions are made for preventing the trouble.

CORRESPONDENCE.

THE DEVELOPMENT OF MINERAL RESOURCES.

To the Editor of the Chemical News.

SIR,—A new branch of the Ministry of Munitions has been established to deal with the examination and development of such mineral properties (other than coal or iron ore) in the United Kingdom as are considered likely to be of special value for purposes of the war. The Ministry of Munitions has appointed the following gentlemen to act as an Advisory Committee on the Development of Mineral Resources:—Sir Lionel Phillips, Bart., Chairman; Mr. J. J. Allan; Mr. C. W. Fielding; Mr. R. J. Frecheville; Prof. F. W. Harbord, F.I.C.; Assoc. R.S.M.; Mr. F. Merricks; Sir Harry Ross Skinner; Dr A. Strahan, LL.D., F.R.S. (representing the Geological Survey); Mr. Edgar Taylor; together with a representative to be nominated by the Board of Trade.

With reference to this announcement, it may be well to point out that the Government of South Australia has for a considerable period provided boring appliances capable of reaching to great depths and bringing up cores of the strata passed through which are in continual use for testing sites for new mineral products, as well as for coal, petroleum, water, &c. This *State enterprise* is a development that could be applied in the United Kingdom with great advantage at the present time. For instance, deep borings could be made in all the known salt localities to ascertain whether potash deposits resembling those at Stassfurt can be found. Droitwich, in particular, seems a likely spot. In the neighbourhood of the Lizard, Cornwall, there are strong surface indications that point to the probable existence of deposits of nickel ore, and possibly of platinum. Near Pately Bridge, in Yorkshire, there are similar indications that make it highly probable that deposits of strontianite, SrCO_3 , underlie the beds of calcite. Well-devised deep borings would no doubt reveal the existence of many other desirable minerals now unutilised which would probably remain dormant and undiscovered if their exploitation is left merely to individual and private enterprise. It would also prove a source of revenue to the Exchequer, as the Government would rightly claim a share in any new discoveries.—I am, &c.,

W. B. GILES, F.I.C.

Ceramic Society.—A meeting will be held at the Central Schools of Science and Technology, on Saturday next, April 14, at 7 p.m. A paper will be read by Mr. S. T. Wilson entitled "The Firing of Pottery Ovens."

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clxiv., No. 2, January 8, 1917.

Spectrographic Studies of Portuguese Uranium and Zirconium Minerals.—A. Pereira-Fojaz.—The author has made an exhaustive study of the composition of specimens of chalcocite, autunite, and zircon from Portugal. Radium was found in the chalcocites from Salugal and Nellas. The sensibility of the line $4682.4 \text{ \AA}$. of radium is apparently greater than that of the stronger line 3814.6 .

No. 3, January 15, 1917.

This number contains no chemical matter.

No. 4, January 22, 1917.

Contribution to the Revision of the Atomic Weight of Bromine. Density of Gaseous Hydrogen Bromide under Reduced Pressure.—C. K. Reiman.—It has already been proved that even very pure dry hydrogen bromide acts on mercury at the ordinary temperature, and hence the compressibility of the gas cannot be measured directly. It can, however, be measured indirectly by determining the density at different pressures. The author has made observations of the density of specimens of the gas prepared by direct combination of its elements, and by the action of phosphoric acid upon KBr. The mean weight of a litre of the gas was found to be 3.6218 grms. in one series of experiments and 3.6330 in another, and hence the atomic weight of bromine was calculated to be 79.924 ($H=1.008$).

Normal Density of Hydrobromic Acid.—W. S. Murray.—The author has prepared HBr by the hydrolysis of Al_2Br_6 . To obtain the aluminium bromide, bromine vapour was allowed to act on aluminium bromide heated to a red heat. The salt was purified by distillation *in vacuo* and then hydrated. On heating the hydrated salt the following reaction occurs:— $\text{Al}_2\text{Br}_6 \cdot 12\text{H}_2\text{O} = \text{Al}_2\text{O}_3 + 6\text{HBr} + 2\text{H}_2\text{O}$. The weight of the normal litre of pure gas was found to be 3.6440 grms.

MISCELLANEOUS.

Faraday Society.—A General Discussion on "Osmotic Pressure" will be held on Tuesday, May 1, 1917, at 8 p.m., in the Rooms of the Chemical Society, Burlington House, W. Sir Oliver Lodge, F.R.S., will preside over the Discussion, which will be opened by Prof. Alfred W. Porter, F.R.S. Dr. F. Tinkler will read a paper on "The Colloidal Membrane—its Properties and its Function in the Osmotic System." Mr. W. R. Bousfield, F.R.S., will read a paper on "Osmotic Pressure in Relation to the Constitution of Water and the Hydrates of the Solute." The following have signified their intention of contributing to the discussion:—Prof. H. E. Armstrong, F.R.S., the Earl of Berkeley, F.R.S., Prof. A. Findlay, Prof. J. C. Philip, Dr. G. Senter, Dr. S. A. Shorter, Mr. W. C. Dampier Whetham, F.R.S.

Iron and Steel Institute.—The Annual Meeting of the Institute will be held, by kind permission, in the House of the Institution of Civil Engineers, Great George Street, Westminster, on Thursday and Friday, May 3 and 4, 1917, commencing on Thursday at 10.30 a.m., and on Friday at 10 a.m. The following is the programme of proceedings:—

Thursday, May 3 (at 10.30 a.m.).

General Meeting of Members.

The Council will present their Report for the year 1916.

The Hon. Treasurer will present the Statement of Accounts for 1916.

Scrutineers will be appointed for the examination of voting papers for election of new Members and Associates of the Institute.

The President will move the adoption of the proposed new By-law for the expulsion of Members, as amended at the Autumn Meeting, for incorporation in the By-laws of the Institute.

Award of the Bessemer Medal for 1917 to Mr. Andrew Lamberton, Vice-President.

A selection of papers will be read and discussed.

Friday, May 4 (at 10 a.m.).

General Meeting of Members.

The award of grants from the Andrew Carnegie Research Fund in aid of research work will be announced.

If time permits some papers may be discussed at any of the Sessions, in which case due notice will be given. Those papers for which time cannot be found will be taken as read, and discussed by correspondence.

The following is the list of papers that are expected to be read:—

L. Grenet (Firmeny, France)—“The Penetration of the Hardening Effect in Chromium and Copper Steels.”

J. N. Kilby (Sheffield)—“Steel Ingot Defects.”

F. C. Langenberg (Harvard, U.S.A.)—“Cementation by Gas Under Pressure.”

G. P. Raidabaugh (Sparrow's Point, U.S.A.)—“Origin and Development of the Railway Rail.” (Being a historical note communicated by the courtesy of the Ebbw Vale Co.).

N. Tschischewsky (Tomsk, Russia)—“Case Hardening of Iron by Boron.”

N. Tschischewsky and N. Schulgin (Tomsk, Russia)—“Determination of the Line S.E. in the Iron-carbon Diagram by Etching Sections at High Temperatures *in vacuo*.”

F. C. Thompson (Sheffield)—“Influence of Surface Tension on the Properties of Metals, especially of Iron and Steel.”

Members intending to take part in the discussion of any of the papers can be supplied with copies a week before the meeting, on application to the Secretary. Copies of all papers will be available at the meeting for the use of Members, and those who are unable to attend can subsequently be supplied, on application, with any paper of which copies remain.

Conduct of Discussions.—A notice indicating the order in which the papers will be taken will be posted up in the Hall of the meeting place. In order that as much time as possible shall be available for discussion, each paper will be read in abstract only, ten minutes being allowed to the author for that purpose, unless otherwise ordered by the meeting. Each speaker will be limited to five minutes in the discussion, unless the time should be extended by unanimous consent. Speakers who are unable in the time available to give more than a summary of their views may send a written statement to the Secretary for publication in the *Journal*. Such statement must be in his hands within a month after the meeting.

The Autumn Meeting will be held, by kind permission of the Council of the Institution of Civil Engineers, at the rooms of that Institution on Thursday and Friday, September 20 and 21.

MEETINGS FOR THE WEEK.

TUESDAY, 17th.—Royal Institution, 3. “Russian Development—The Old Free Russia,” by Prof. C. R. Beazley.

THURSDAY, 19th.—Royal Institution, 3. “Industrial Finance after the War—The Character of the Industrial Struggle of To-day,” by Prof. H. S. Foxwell.

FRIDAY, 20th.—Royal Institution, 5.30. “The Future of Wheat-growing in England,” by Prof. R. H. Biffen.

SATURDAY, 21st.—Royal Institution, 3. “Principles of Aerial Navigation,” by Prof. G. H. Bryan.

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THE CHEMICAL NEWS

VOL. CXV., No. 2995.

GRAVITATIONAL ATTRACTION.

By F. H. LORING.

THE mutual attraction of matter either within its self-same mass or across intervening space which as far as can be found possesses no corresponding magnetic field, nor contains any other linking device, has been a profound mystery. The law of attraction is well known, but no connecting mechanism has been discovered.

The general fact of gravitation is simple, namely, "that between every pair of material particles there exists an attractive force which is proportional to the product of the masses of the two particles, and to the reciprocal of the square of the distance between them" (Risteen). Put in another way, it may be stated that all material bodies attract each other, and taking for convenience pairs, the attractive force is proportional to the product of their masses and the reciprocal of the squares of their distances apart, the bodies being considered as shrunk to points when taking the distances between them.

In some respects magnetic attraction seems intimately related to gravitational attraction, and it is suggested that both are of common origin.

Starting with magnetic phenomena, opinion differs as to the physical interpretation of magnetism, one school of thought holding that since a magnetic field has both *direction* and *intensity* it can be truthfully represented by actual lines of magnetic force, the number taken representing the intensity.

The other school considers this idea too descriptive, and they say it is only the mathematical relationships which are known, and these do not themselves justify such a physical interpretation.

Magnetic phenomena, however, give colour to the physical theory in question, and it is largely held that the lines-of-force conception is so near to the actual truth that a literal interpretation is possible without leading to error in practice.

The magnetic field round a current-bearing conductor may be represented in the usual manner by concentric encircling lines, and the fact that these lines are influenced by neighbouring lines of another like current-bearing conductor in such manner that they become mutually distorted leads to the belief that, however much two or more fields encroach on each other, the lines are crowded together but not necessarily annihilated; yet, in effect they neutralise each other where their directions do not coincide, that is to say, where they are superposed whilst in opposition.

A circular group of current-bearing conductors (arranged in squirrel-cage fashion) may be so far apart as not to give rise to any appreciable distortion of the magnetic lines, and therefore involve no consequent neutralisation—this latter term to be taken to have a particular meaning presently.

In order to study the behaviour of the lines of force, the wires may be slowly moved together, so as to consolidate them eventually into a solid round rod, the field gradually changing *until complete radial neutralisation takes place*: wherein lies a new or extended conception of the character of magnetic lines of force when it is understood that the term *neutralisation* as here used may be defined as a phenomenon resembling the neutralisation of an acid with an alkali, in that the components are not annihilated. This will be better understood from what follows.

Consider the wires thus consolidated into a homogeneous rod and consequently the neutralisation being

along radial lines extending from the centre of the rod, whilst at the turning points or places the lines may form *resultant* ones. It is to be noted that the turning places widen in proportion to the distance taken from the conductor. The original wires may be considered as shrunk to atomic or molecular thinness when tracing the effect back to its elemental origin.

The circular lines taken external to the conductor are therefore supposed to be made up from the radial loops, the former being resultant lines as shown by the accompanying diagram.

If the lines of force are not annihilated, then either two or more forces occupy the same place, or the opposing lines are closely packed together. Force is not a *thing* in the accepted material sense, but a magnetic field has such characteristics as to lead one to suspect that whatever the field may be, there is an intensity of action which behaves to material bodies of a certain kind (a moving mass of copper for example) as if there was a medium present. In all probability the action of forces may be regarded as perfectly superposable without individual destruction, and thus they become differentiated from matter, though forming in a sense a part thereof, just as the momentum of a body is bound up with it, but can have no value until the body is moved.

In the above case there is a certain condition of affairs assumed that resembles gravitational attraction, in that the neutralised lines of force disappear to all intents and purposes; and, if a plastic iron tube or ring were arranged to surround a current-bearing wire, being placed concentrically to it with an annular intervening space, the iron would be expected to contract on the wire when the circuit was established, just as if the wire attracted it gravitationally. This, of course, is a purely hypothetical case, as the iron would have to retain its magnetic property and yet remain pliable.

The hypothetical iron would be the seat of a strong magnetic flux (assuming considerable current passing through the central conductor), and according to the usual conception it would be said that the closed lines in the iron were like stretched elastic bands and tended to contract upon themselves and thus force the plastic iron to collapse or extend itself to the wire. If the iron accommodates or induces a greater total flux in a given position, it will retain that position, but if in a new position it will accommodate or induce more lines, the iron will endeavour to take up such a position.

The movement of the plastic iron towards the wire is a case of action at a distance due to the magnetism yet without any intervening cross magnetic field that can be detected as such. It would appear that the wire was attracting the iron in a gravitational manner, since no extraneous radial magnetic field would be discernible.

If now the principle of neutralised lines in the chemical sense (see above) be accepted, then these lines are the ones which are in reality causing the iron to move towards the wire, unless the lining-up of the molecules or atoms in the iron contributes overwhelmingly towards the elastic-band effect: due to an increased number of lines, the permeability of the iron being very high.

Whatever action takes place, the idea of neutralised lines affords a second-order effect, which might provide a means of explaining or in some way elucidating gravitational attraction without introducing any new basic conception other than that of the magnetic field interpreted in an extended way.

Accordingly, gravitational attraction might be taken as a sort of superposed magnetic effect, the intervening lines of magnetism being neutralised but still there and functioning as elastic bands or filaments interlinking or uniting all matter.

It is to be further noted that probably the plastic iron will be attracted wirewards regardless of the direction of the central current, thus leading to the supposition that attraction would follow even if the current were to flow simultaneously in opposite directions. That the attraction

would be exceedingly small in such a case seems probable, since opposing currents in side-by-side conductors, though in a sense equivalent to a single-direction current of equal total amperage, would not induce any molecular or atomic rearrangement in the iron, consequently there would be no organised flux therein.

Since therefore, direction plays no absolute part in the secondary, or second-order effect, a linear or organised current would not be necessary, and it seems probable that molecular or atomic currents would meet the case, these currents taken collectively being heterogeneous.

The weakness of the gravitational field in comparison with a magnetic field supports the idea that the neutralisation effect reduces the magnetic effect to one of a second order, and therefore great masses are necessarily involved in obtaining appreciable attraction.

This argument, or rather the extended interpretation of well-known phenomena, leads to the supposition that lines of magnetic force are never destroyed, but only brought into requisition by the artifice of the experimenter, or by the device of the engineer. Moreover, the second-order effect would be expected rather than a first-order one, but the circumstance of inducing a magnetic flux in a ring of iron or steel would not perceptibly lessen its weight. The mass of the earth is so great compared with, say, a magnetised ring, that the former would be expected to contribute the effective lines in proportion to its mass; consequently, whatever contribution there may be from the magnet it would be negligible by com-

parison, and it would probably be impossible to detect any difference in weight even by means of a sensitive balance. It is assumed that organising the lines of the magnet would prevent them functioning in a gravitational capacity.

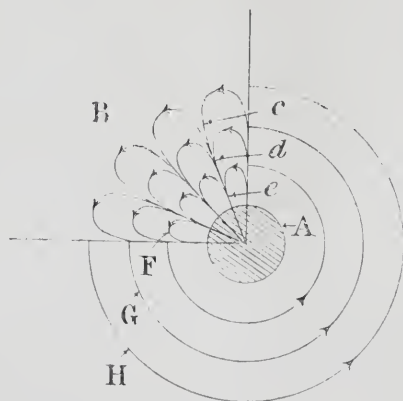
is demanded of any lines that function in a gravitational capacity. Electrostatic lines are, by the way, ruled out of consideration, as a basis for gravitational attraction, because they are stopped by metallic surfaces. According to this hypothesis, therefore, gravitational attraction might be defined as a second-order magnetic effect whereby the lines of magnetic force are neutralised so far as any manifestation in the gravitational field is concerned, but these lines being in the field or in intervening space and having on origin in the atomic currents in the masses of matter involved, proportionate to their conjoint masses, give rise to a binding attraction by virtue of the inherent property of magnetic lines to act as stretched elastic bands. This leads to the magnetic field round a conductor being made up of radial elements substantially as illustrated by the diagram.

That the lines have an origin in the atomic currents may be more apparent than real, since the neutralised lines of force may represent a property of space, the atoms serving as anchoring media.

Faraday, to whom we owe the conception of lines of force, thought that all space contained such lines, and we know that the magnetic field of the earth is an example of magnetic lines on a large scale. Faraday also had in mind electrostatic lines which are not under consideration except in so far as a moving charge gives rise to a magnetic field (Rowland).

In attempting to visualise these lines of force in their bewildering maze of complexity the mind reels at the thought, but this idea may be a comparable counterpart to the marvel of the electro-atomic structure of matter itself. The peopling of all solid, liquid, and gaseous bodies with live electrons is difficult to comprehend. Each atom is, in fact, a miniature planetary system, and the revolving negative electrons give in effect the atomic currents mentioned above. The number of such systems in the smallest speck of dust discernible, and that this dust particle will fall to earth by reason of that which is linked up to it and extending far beyond its confines, are equally difficult of realisation.

The whole conception rests upon an hypothesis of force lines, the extent and nature of which involves thinking of them in terms distinct from those of matter, very much as the modern principle of relativity becomes an extension of thought beyond that of classical relativity. For an interesting phase of the relativity philosophy Minkowski's world lines become of interest. See Silberstein's "Theory of Relativity" (Macmillan, 1914), pp. 129-131. Quite apart from the relativity conception, a thing is not complete from the point of view of this hypothesis if specified in terms of three dimensions, because it is linked up with other things, hence a fourth dimension seems necessary: one implying volume extension. A charming paper on the "Fourth Dimension," by Eleanor Beatrice Harvey (*Trans. Rochdale Literary and Scientific Soc.*, 1912, xl., 5-17), though not giving exactly this idea is highly suggestive.



A = Section of a current-bearing conductor.

B = An enlarged group of radial line-elements (loops).

c, d, and e = Places where radial "neutralisation" takes place.

f, g, and h = Resultant lines as a consequence of the "elements."

parison, and it would probably be impossible to detect any difference in weight even by means of a sensitive balance. It is assumed that organising the lines of the magnet would prevent them functioning in a gravitational capacity.

It might be possible to devise an experiment somewhat along the lines of Dr. Shaw's experiment (a brief mention of the latest contribution by Shaw and Hayes is given in the *CHEMICAL NEWS*, cxv., p. 116), which should, according to this hypothesis, show a difference in attraction when a ring of iron or steel is highly magnetised.

There are several interesting developments which are not in conflict with the hypothesis. The shielding action of iron towards magnetic lines is evidently due to the organised flux therein, and such a flux is differentiable from the resultant lines that may be developed in space or practically non-magnetic media, the former not being resultant lines in the same sense though inducible by the latter. The iron flux, for example, is a molecular or atomic phenomenon of self-contained origin within the iron. The neutralised lines, moreover, pass, for instance, through iron the same as through brass, and this property

AN ELEMENT WHICH COMES DOWN IN THE IRON GROUP.

By W. BRAMLEY.

1. Not precipitated by H_2S in acid solutions.
2. Oxalic acid, no precipitate.
3. Ammonia, a white precipitate, insoluble in excess.
4. Ammonium carbonate, white precipitate, soluble in excess, reprecipitated by boiling.
5. Sodium carbonate, white precipitate, insoluble in excess.
6. Potassium hydrate, white precipitate, insoluble in excess.
7. Bicarbonate of soda, white precipitate, soluble in excess.

8. Thiosulphate of soda, gives a white precipitate on heating the solutions to boiling.
9. Ferrocyanide of potassium, gives in acid solutions a yellowish precipitate, decomposed by ammonia, leaving a white precipitate of the hydroxide.
10. Ferrocyanide of potassium, gives no precipitate in neutral solutions.
11. Strong solutions of sulphate of potash (hot or cold), give a white precipitate, easily dissolved by cold dilute HCl.
12. Strong solution of sulphate of soda, give no precipitate.
13. Barium carbonate, gives a white precipitate quickly and completely in cold solutions.
14. When the sulphate is diluted to 200 cc. and boiled, a white precipitate of the basic sulphate is thrown down.
15. When the sulphate is diluted, with the previous addition of 4 or 5 cc. of strong HCl, to 200 cc. and boiled, the same precipitate is obtained.
16. When a solution of the chloride is evaporated to dryness and redissolved in a small quantity of strong HCl by heating, a crystalline mass is obtained on cooling.

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EXPERIMENTS UPON STARCH AS SUBSTRATE FOR ENZYME ACTION.*

By H. C. SHERMAN and J. C. BAKER.

(Continued from p. 178).

Experiments upon Potato Starch Prepared in the Laboratory.—For the main series of experiments, starch was prepared in the laboratory from mature August potatoes, with care to prevent contamination by organisms, dust, fumes or water containing electrolytes. Pastes made by heating this starch in pure water could not be separated by centrifuging as described above. Experiments were then made to test the effect of adding small amounts of known electrolytes to the starch paste before centrifuging, and it was found that the addition of a very small amount of hydrochloric acid or sodium chloride sufficed to ensure a good separation. Since sodium chloride (at least in small amounts) is known to have no injurious effect upon amylolytic enzymes its use was decided upon, and in all subsequent centrifugal separations of 1 per cent starch pastes enough sodium chloride was added to bring the concentration of salt in the final mixture to 0.001 M. When 2 per cent starch pastes were to be separated a 0.002 M concentration of salt was employed.

The effect of varying the time and temperature of heating was studied in repeated experiments, in all of which the paste resulting from dispersion of the starch was separated by the centrifuge in the manner already described, the centrifugate filtered through filter-paper covered with a thin layer of cotton, and the concentration of starch material in the filtered centrifugate was determined by evaporating and drying to constant weight at 80° in *vacuo*. These experiments showed that the bulk of the readily soluble material was extracted from the starch grains very quickly by water at 70–80°. When one part of starch suspended in thirteen parts of cold water was poured into eighty-seven parts of water heated sufficiently to give the entire mixture the desired temperature and containing sufficient salt to give the desired final concentration, thoroughly stirred for at least one minute until the viscosity no longer seemed to increase, and the paste then centrifuged as promptly as practicable (within ten minutes of the first exposure of the starch to the hot water) the

concentration of amylose in the centrifugate was about the same as when the heating was continued for one hour. Prolonged heating (up to thirty hours) caused a very slow gradual increase in the amount of material going into the filtered centrifugate. Thus the concentration after heating at 80° for ten minutes to one hour averaged 0.20 per cent; after nineteen hours, 0.30 per cent; after thirty hours, 0.35 per cent.

In several cases the lower layer from the centrifugal separation was again treated with hot water and centrifuged a second and a third time, and the material thus extracted was compared as to amount and iodine reaction with the residual material and with the material of the first centrifugate. In this way it was found that the material brought into solution by repeated treatment with hot water, and, therefore, presumably the material which comes slowly into solution on prolonged heating with large excess of water, is different from that contained in the first centrifugate (original upper layer), and apparently consists of a mixture of the β -amylose, which constitutes the chief solid of the upper layer, and the α -amylose, which is the chief solid of the lower layer or residual gel.

To develop a given intensity of blue colour with iodine requires from thirteen to eighteen times as much of the twice-washed solids of the residual gel (crude α -amylose) as is required of the solids of the original centrifugate (crude β -amylose); or, in other words, the solid matter of the β -amylose fraction had thirteen to eighteen times the blue-forming property of the solids of the α -amylose fraction, and the solids of the washings (second and third centrifugates) were of intermediate character.

(NOTE.—It is hardly necessary to say that in speaking of this as a property which helps to differentiate the two fractions, we do not mean to convey the impression of a definite chemical reaction in either case).

No attempt was made to investigate the exact significance of these differences, which we recognise to depend to a considerable extent upon the amount of iodine arbitrarily chosen by Wohlgemuth for making such tests, because for the purposes of this investigation it was desired that the material going into the substrate should be as nearly homogeneous and as little changed from the form in which it exists in the natural starch as is possible. For these reasons it was decided to use in the separation of β -amylose only a short exposure of the starch to hot water, as described above, centrifuging within ten minutes, and determining the solids in the centrifugate after filtering as already explained. Experiments at different temperatures indicated that the best results were obtained in heating at 75° in the preparation of 2 per cent, or 80° in the preparation of 1 per cent pastes.

The viscosities as influenced by heating and by treatment with acid or alkali also furnish evidence of a pronounced difference between the substances contained in the two layers separated by the centrifuge, the " β -amylose" of our fractionation resembling the "amylose" of Gruzewska and of Samec in this respect and differing greatly from the α amylose fraction ("amylopectin").

Thus in an experiment in which the filtered β -amylose layer as obtained had a concentration of 0.4 per cent and a viscosity of 1.13 the α -amylose layer, when diluted to the same concentration, showed a viscosity of 1.18. On heating the β -amylose solution its viscosity was lowered to 1.03 after five minutes' and 1.02 after twenty minutes' boiling. Boiling the α -amylose solution of the same concentration for five minutes raised its viscosity to 1.38, and heating for one hour in the autoclave at 125° increased it to 1.81; further heating in the autoclave caused decrease of viscosity—to 1.13 at the end of two hours and 1.12 at the end of three and a-half hours' heating at the same temperature. (For discussion of effect of heat treatment upon viscosities of starch solutions, see Harrison, *Journ. Soc. Dyers and Colourists*, April, 1911).

The addition of sufficient hydrochloric acid to give a concentration of 0.02 N did not change the viscosity of a β -amylose solution, and sodium hydroxide in equivalent

* From the *Journal of the American Chemical Society*, xxxviii., No. 9.

concentration increased the viscosity only slightly. This is in accordance with the results of Samec (*Koll. Beihefte*, iv., 132; vi., 32), who finds that the viscosity of a starch solution (chiefly α -amylose) is decreased by hydrochloric acid and increased by sodium hydroxide to a very marked extent, while the viscosity of a solution of "amylose" (β -amylose) prepared by his modification of Gruzewska's method was not appreciably affected.

The two fractions into which starch is divided by the process above described and which, although not quantitatively free from each other, are for convenience referred to simply as α - and β -amylose, also differ from each other in their behaviour as regards *retrogradation*. We have had no evidence of retrogradation in any of our α -amylose solutions, while the β -amylose solutions show the phenomenon to a pronounced degree, the more so the lower the temperature or the higher the concentration.

In an experiment to test this property β -amylose solutions of 0.6 and 0.2 per cent were allowed to stand in the refrigerator for three weeks and were then filtered. The filtrates contained only 0.04 and 0.037 per cent, respectively. The completeness of this retrogradation is a further indication of the identity of this material with Gruzewska's amylose (*Comptes Rendus*, 1911, clii., 785). It seems not improbable that in ordinary starch pastes the α -amylose may act as a protective colloid to the β -amylose. In all of the cases observed by us the retrogradation of the β -amylose has occurred more readily in the absence than in the presence of amylase, the enzymes being employed in purified form and low concentration. The suggestion that the amylase may exert a coagulating influence upon the substrate seems superfluous, at least as regards enzymes of the degree of purity used in these experiments. The phenomena observed by Maquenne and Roux and attributed by them to an amylcoagulase may possibly have been due to the digestion of α -amylose and consequent removal of its protective effect upon the β -amylose.

In order to avoid retrogradation in our digestion experiments the solutions were autoclaved, allowed to cool to 40° and then promptly mixed with the enzyme solution, the activating salts being added at the same time (not mixed with the substrate in advance). Omission of such precautions is likely to result in cloudy digestion mixtures and delayed iodine end points.

The phosphorus content of the two fractions separated by the centrifuge was studied as a further indication of the relative amounts of α - and β -amyloses and the extent to which they are differentiated by the procedure here used.

According to Samec, the phosphorus of starch is all contained in the α -amylose ("amylopectin") portion. If, then, the centrifuge separates the α - and β -amylose, the phosphorus should be found in the lower layer; but since in Northrop and Nelson's experiments (*Journ. Am. Chem. Soc.*, 1916, xxxviii., 472) about one-tenth of the phosphorus escaped recovery, it is possible that the α - and β -amyloses might be separated by the centrifuge and still a fraction up to 10 per cent of the original phosphorus might be found in the upper layer or diffused throughout the dispersion medium. In several experiments in which we have determined the phosphorus, the centrifugates (upper layers) constituting about 70 per cent of the total volume have never contained more than about 2 per cent of the total found. Our results are thus in harmony with the findings of Northrop and Nelson and with the view that α - and β -amylose ("amylopectin" and "amylose") are separable by heating with water and centrifuging as here described.

The amounts of phosphorus found in the β -amylose fraction are but little, if any, above the limits of experimental error, and for most purposes might be regarded as negligible, but since the concentration of solids in this layer is only about 0.20 per cent the percentage of phosphorus in the solids is about one-tenth as high for this fraction as for the whole starch, so that it seemed desirable

to ascertain, if possible, whether the phosphorus of the β -amylose layer were present merely as diffusible phosphate or in the form of α -amylose or other non-diffusible material.

The centrifugates (β -amylose layers) from several experiments were saved and united, a portion of the solution reserved, and the remainder dialysed in a collodion bag against five to eight times its volume of redistilled water for eight days, the water being changed every day. A portion of the centrifuge residue (α -amylose layer) was diluted to a similar concentration and dialysed under the same conditions. With the kind assistance of Dr. I. Greenwald, of the Hariman Research Laboratory, the phosphorus content of these solutions was determined nephelometrically by precipitating as strychnine phosphomolybdate according to the method of Pouget and Chouhach (*Bull. Soc. Chim.*, 1909, [4], v., 104; 1911, ix., 649). The β -amylose layer showed before dialysis 0.00002 per cent and after dialysis 0.00001 per cent of phosphorus; the α -amylose layer after dilution to corresponding concentration of solids showed 0.00195 per cent before, and 0.00180 per cent after dialysis. Thus the eight-day dialysis had removed half of the phosphorus of the β -amylose layer and somewhat less than one-tenth of that of the α -amylose layer. Calculating the phosphorus in percentage of the starch solids present it is found before dialysis to constitute 0.068 per cent of the α -amylose fraction and 0.010 per cent of the β -amylose fraction, or about one-seventh as much in the latter case as in the former. If the phosphorus were assumed to be present only in the form of α -amylose it would follow that the amylose of the upper layer from the centrifuge is about one-seventh α -amylose and six-sevenths β -amylose; but since at least half of the phosphorus of this fraction is dialysable it appears probable that well over nine-tenths of the starch material in the upper layer from the centrifuge tube is β -amylose (using this term to designate the phosphorus-free fraction of starch which gives a pure blue reaction with iodine). From the comparison of iodine colour reactions and solubilities it also appears probable that the starchy material of the lower layer after separation and two washings in the centrifuge is at least nine-tenths α -amylose.

Thus it appears that by the method of regulated dispersion and centrifugal separation here described it is feasible to divide potato starch into two fractions, one of which is more than nine-tenths α -amylose and the other more than nine-tenths β -amylose. If amylases behave differently toward α - and β -amylose it should be possible to study their differences in behaviour by experiments in which these two fractions are used side by side as substrates for the action of the enzyme. The data recorded below are typical of those which we have obtained in several series of comparative experiments of this sort.

Experiments with Enzymes.

In the experiments with enzymes recorded in this paper we have used each enzyme in the presence of its optimum concentration of salt and phosphate as determined in previous work in this laboratory.

Except as different enzymes with their appropriate activators were used, the only variable factor was the nature of the substrate. All digestions were conducted at 40° with all the precautions as to purity of reagents and water used, and accurate control of time and temperature, which have been described in previous papers (*Journ. Am. Chem. Soc.*, xxxii., 1073, 1087; xxxiii., 1195; xxxv., 1617; xxxvii., 623). The enzyme hydrolysis of four potato starch substrates— α - and β -amyloses, Lintner soluble starch, and whole starch autoclaved—has been studied at two concentrations of substrate, 0.16 per cent and 0.5 per cent. For the sake of brevity only the latter will be described.

Preparation of Substrates.—The α -amylose substrate was prepared by centrifuging a 1 per cent starch paste made at 85° in a concentration of 0.001 M sodium chloride as previously described. The supernatant β -

TABLE II.—Hydrolysis of different Substrates by Commercial Pancreatic Amylase (Pancreatin 6).

Time.	Soluble starch.		Autoclaved starch.		α -Amylose substrate.		β -Amylose substrate.	
	Maltose in terms of theory. Per cent.	$k \times 105$. (a)	Maltose in terms of theory. Per cent.	$k \times 105$.	Maltose in terms of theory. Per cent.	$k \times 105$.	Maltose in terms of theory. Per cent.	$k \times 105$.
30 minutes	4.3	63	4.3	63	4.6	67	5.2	77
60 "	8.4	63	8.5	64	7.7	58	10.7	81
90 "	12.5	64	13.0	67	11.2	57	15.2	79
120 "	16.2	64	17.5	69	14.9	58	20.1	82
150 "	20.0	64	21.0	68	18.4	58	25.6	85
180 "	23.0	63	24.4	69	21.2	57	31.3	91
210 "	26.7	64	28.1	68	24.4	57	35.6	91
240 "	29.5	63	31.1	67	26.9	56	39.9	92
6 hours	38.6	58	40.2	62	35.6	53	52.4	91
18 "	56.2	33	58.0	34	52.8	30	75.2	56
24 "	59.3	26	61.2	28	56.9	25	77.5	45

TABLE III.—Hydrolysis of different Substrates by Purified Pancreatic Amylase (Preparation 59).

30 minutes	4.4	65	4.2	62	6.1	91
60 "	10.8	83	7.5	56	11.3	87
90 "	13.1	67	11.4	58	16.8	86
120 "	17.0	67	14.9	58	22.6	93
150 "	21.9	71	18.0	57	28.2	96
180 "	25.7	72	21.0	57	33.7	99
210 "	28.8	70	24.0	57	38.7	101
240 "	31.5	68	26.5	56	43.2	102
6 hours	39.0	59	34.8	51	55.0	96
24 "	59.4	27	55.1	24	81.5	56

(a) From the formula $(1/t \log a/a - x = k)$, in which t = time in minutes, a = the amount of maltose theoretically obtainable (starch $\times 1.05$), and x = maltose found at time t .

amylose layer was decanted off and an equal volume of hot 0.001 M sodium chloride stirred into the α amylose layer and this again centrifuged. This washing was repeated and the residue then diluted to the original volume, and this solution (about 0.8 per cent) heated in autoclave at 125° for two and a half hours. The exact concentration was then determined by evaporating a portion *in vacuo* at 80°. When about to start an experiment, this solution was sufficiently diluted with water, so that when mixed with the activator and enzyme solutions the desired final concentration of 0.5 per cent substrate would be obtained.

The β -amylose substrate was prepared by centrifuging a 2 per cent starch paste prepared at 75° containing sodium chloride in 0.002 M concentration. The supernatant liquid from the centrifuge tube was filtered through paper covered with a thin layer of absorbent cotton. About 170 cc. of 0.4 per cent filtered β -amylose solution were obtained from 400 cc. of 2 per cent starch paste. Two such filtrates were usually united. A portion of this solution was evaporated *in vacuo* at 80° to determine the exact concentration of β -amylose and a larger measured volume (sufficient for the experiment contemplated) was concentrated by evaporation to about 0.8 per cent autoclaved in the same manner as the α -amylose solution and finally brought exactly to the desired concentration.

"Autoclaved starch" was prepared by heating a 0.8 per cent starch paste in the autoclave as described under α -amylose, and then bringing to the proper concentration.

"Soluble starch" (Lintner) was "dissolved" by boiling with water for ten minutes and was not heated in the autoclave.

The initial reducing power of each substrate was determined and this value subtracted from that found in the digestion experiments.

Each digestion experiment was started by measuring the enzyme solution into a flask and pouring into it the proper volumes of substrate solution and of the solution of

activating salts, so that the concentration of substrate in the final digestion mixture was exactly 0.5 per cent. The substrate and activator solutions were measured at 40° and this temperature was maintained throughout the experiment, portions being withdrawn by pipette from time to time without removing the main solution from the thermostat.

The four experiments of a set were started at intervals of one minute so that portions of each might be withdrawn in succession after exactly equal digestion periods. Each measured portion as withdrawn was at once delivered into a flask containing mixed Fehling solution, and the reducing sugars determined at once, following the procedure described by Sherman, Kendall, and Clark (*Journ. Am. Chem. Soc.*, 1910, xxxii., 1072) and calculating the result as maltose by means of Deffen's table (*Ibid.*, xviii., 749). In order to simplify the tabular statement and comparison of the results, the weights of reduced copper and the corresponding weights of maltose are omitted, and only the maltose as calculated in terms of the amount theoretically obtainable from the substrate and the corresponding velocity constant are printed. Since it has been shown (Sherman and Punnett, *Ibid.*, 1916, xxxviii., 1877) that even purified amylases may form appreciable amounts of glucose as well as maltose, it is possible that the figure for maltose calculated from the reduction of Fehling solution may, in prolonged digestions or under special conditions of enzyme or substrate, exceed the theoretical yield.

Action of Pancreatic Amylase.—The four substrates above described were quantitatively compared as regards their digestion by pancreatic amylase, first in the form of a high grade commercial pancreatin (Pancreatin 6) and then in the form of a highly purified laboratory preparation (Preparation 59). The results are shown in Tables II. and III. respectively.

It will be seen that under the action of pancreatic amylase, whether in commercial or purified form, the yield of reducing sugar is higher for the β -amylose than for

the α -amylose fraction at each of the stages at which the digestion mixture was tested, the difference becoming greater as the digestion proceeds. The amount of enzyme here used was small in order that the progress of the reaction might be slow enough to be followed experimentally through the earlier stages. Under these conditions, at the end of twenty-four hours, when the last of the digestion mixture was withdrawn for testing, the reaction was still in progress, and the yield of maltose had reached in the two series of experiments respectively only 56.9 and 55.1 per cent of theoretical in the α -amylose and 77.5 and 84.5 per cent in the β -amylose fraction.

Since each of the successive reactions by which maltose is formed is an hydrolysis taking place in water solution, and therefore essentially a unimolecular reaction, and it is the catalytic effect of the enzyme which causes these reactions to proceed at a measurable rate, it follows that the speed of formation of maltose may be expressed in terms of k of the unimolecular reaction formula—

$$(\tau)t \log a(a - x) = k,$$

and that (under a given set of conditions, as in either one of the two sets of experiments here described) the magnitude of k at any given stage in the experiment may be regarded as an indication of the efficiency with which the formation of maltose is catalysed at that stage. Constancy of k from the beginning of the experiment until a practically theoretical yield of maltose is obtained would indicate that the group of hydrolyses which produce maltose (that of starch and of each of the resultant dextrins) is equally catalysed by the enzyme throughout; whereas if the digestion yields at any stage a dextrin which is less readily hydrolysed by the enzyme, the value of k must diminish. A fall in the value of k may therefore serve as an indication of the formation of a "resistant dextrin." When equal amounts of the same enzyme act on equal amounts of different substrates under identical conditions, a comparison of the values for k may indicate an earlier or a larger production of "resistant dextrin" from one substrate than from the other.

The data in Table II. show in all cases a decided diminution of the velocity of reaction (expressed as value of k) between the sixth and the eighteenth hour. Comparing the yields of maltose from the different substrates at these periods it is plain that the decrease in the value of k began at a lower yield of maltose in the α -amylose than in the β -amylose fraction, indicating that the former yields more of the relatively resistant dextrin than the latter, or that its dextrin is more resistant than the corresponding dextrin from β -amylose. Lintner soluble starch and autoclaved whole starch gives intermediate results, but approach the behaviour of α -amylose more closely than that of β -amylose, as is consistent with the other evidence that they consist much more largely of the former than of the latter.

Similar comparison of the data obtained in experiments with other amylases described below will show that the stage of digestion at which the value of k begins to diminish depends upon the enzyme as well as the substrate, but that in all cases the indications of "resistant dextrin" are much more pronounced in the α -amylose than in the β -amylose fraction.

There are, of course, many causes which may contribute to the slowing of the reaction as the hydrolysis proceeds, such as the destructive action of water upon the enzyme, inactivation of enzyme by combination with hydrolytic products, &c. Without entering into discussion of such factors here, it may be pointed out that the arrangement of these experiments was such that any distinctly different behaviours of k in experiments recorded in any one table (such as discussed in the above paragraph referring to Table II.) may be interpreted as due to some difference in the substrate or its hydrolytic products. The general relations noted from the data of Table II. will be seen to hold true for those of Table III. also.

(To be continued).

OBSERVATIONS ON THE RARE EARTHS.*

By EDGAR W. ENGLE† and CLARENCE W. BALKE.

I. *Introduction.*—One object of the present work was to study some separation methods which might be suitable for the isolation of the various individual rare earths, more particularly those of the yttrium group. This was undertaken preliminary to a later object which was to prepare dysprosium material of sufficient purity for atomic weight work, and to determine the atomic weight of that element. Oxides of the rare earths obtained from a previous investigation furnished most of the material for this work (Egan and Balke, *Journ. Am. Chem. Soc.*, 1913, xxxv., 365). These were originally obtained from the following mineral sources:—Monazite, gadolinite, xenotime, euxenite, and fergusonite. From the gadolinite and xenotime material part of the yttrium had been previously removed in the investigation above referred to. The oxides were, in the main, those of the yttrium earths, though some portions contained appreciable quantities of the cerium earths.

II. *Separation of Cerium and Yttrium Groups.*—For the separation of the earths the scheme suggested by James was used as a working basis (*Journ. Am. Chem. Soc.*, 1908, xxx., 979; 1912, xxxiv., 757). However, several deviations were made from this scheme. The method used for the separation of the yttrium earths from the cerium earths depends upon the fact that the cerium earths are but slightly soluble in a saturated solution of sodium or potassium sulphate, while, in the presence of the cerium earths, the yttrium earths are quite soluble in these solutions. This separation, which is approximate and which serves to divide roughly the rare earths into the two groups, was carried out as follows:—The oxides were dissolved in strong nitric or hydrochloric acid, a large excess of acid being avoided. The solutions were diluted with water so that there was a volume of about 1 litre for each 100 grms. of dissolved oxide. Solid sodium or potassium sulphate was added, and the solutions stirred from time to time until they were saturated with the alkali sulphate, or until the absorption spectra showed the removal of most of the cerium earths from solution. Ordinarily this process required three or four days. The solutions were kept cool in order to reduce to a minimum the amount of alkali sulphate required. One portion treated with sodium sulphate consisted of the chlorides from 3760 grms. of oxides, mainly cerium group, obtained from oxalates furnished by the Welsbach Company. The solution was filtered, diluted, and precipitated in the cold with oxalic acid. The precipitated oxalates, which probably carried down slight amounts of sodium oxalate, were washed and ignited to oxides (Baxter and Daudt, *Journ. Am. Chem. Soc.*, 1908, xxx., 563). The oxides weighed 490 grms.

In most of the other portions treated the cerium group material formed only a small percentage of the whole, and the amounts precipitated by the alkali sulphates were less. The alkali sulphates carried down some yttrium group material with the cerium earth precipitate. When the precipitation was complete the solutions were decanted through a filter, the precipitate washed a few times with a saturated solution of the alkali sulphate, and set aside for later treatment. The filtrates were diluted with water, and the earths precipitated with a hot saturated solution of oxalic acid. The oxalates obtained settled rapidly, and could be washed easily by decantation. After having been washed until the alkali salts in solution were removed the oxalates were sucked dry on a Büchner funnel. Part of the oxalates obtained in this way were ignited to oxides, dissolved in nitric or hydrochloric acid, and reprecipitated with oxalic acid. The oxalates were washed again in order to remove alkali salts which might have been included in the first precipitate. If these are not removed

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† This paper represents part of the work done by Edgar W. Engle in fulfillment of the requirement for the degree of Doctor of Philosophy in the Graduate School of the University of Illinois.

TABLE I.

Fraction No.	Colour.	Absorption shows.	Earths present.
8	Almost colourless	Sa, Nd	Sa, Gd, Nd
9, 10, 11	Pink	Sa, Nd	Sa, Nd, Gd
12, 13	Flesh-pink	Nd, Pr, Dy, Ho	Nd, Pr, Dy, Ho
14, 15	Yellowish pink	Nd, Pr, Dy, Ho	Nd, Pr, Dy, Ho, Y
16, 17	Cream	Dy, Ho	Dy, Ho, Y
18, 19, 20, 21	Pale pink	Er	Y, Er
22, 23, 24, 25, 26, 27	Pink	Er	Y, Er
28	Yellowish pink	Er, Tm	Y, Er, Tm
29, 30	Greenish yellow	Er, Tm	Er, Tm
31	Bright blue-green	Tm	Tm

they cause inconvenience in the later fractionation of the earths.

III. *Fractionation of the Bromates.*—For the preliminary separation of the yttrium group elements the bromate method, first proposed by James, was chosen as being the most satisfactory (*Journ. Am. Chem. Soc.*, 1908, xxx., 182; *CHEMICAL NEWS*, 1908, xcvi., 61). The rare earth bromates are best prepared in quantity by the double decomposition of rare earth sulphates and barium bromate. The oxalates of the rare earths may be changed to sulphates either by igniting to oxide and dissolving the oxide in cold dilute sulphuric acid, or by making the oxalates into a paste with a slight excess of concentrated sulphuric acid and igniting to drive off the excess of acid. The latter method was found more satisfactory. The sulphates obtained by this method were dissolved in ice-cold water by adding slowly with constant stirring. The sulphate solution was added slowly to an excess of hot barium bromate solution contained in a porcelain evaporating dish of 65 litres capacity. The liquid in the dish was kept agitated by means of a mechanical stirring device. The solution containing the rare earth bromates, along with a slight amount of barium bromate was drawn off from time to time, and more barium bromate and earth sulphate added as required. The bromate solution was pale pink in colour, and the solid bromates had a light pink colour.

The bromates were fractionally crystallised for a long time in the usual way. Eighteen-inch evaporating dishes were used for containers at first. However, as the number of fractions increased and the size of each became correspondingly small, smaller dishes were used, and as soon as size permitted the fractions were transferred to 3-litre Jena flasks, Florence shape, and finally to smaller ones. In some of the later series of fractionation flasks of 50 cc. were used. For a rather large series flasks of 700 cc. capacity were found very convenient to handle. Flasks have advantage over casseroles in that creeping of the material is eliminated, the solutions lend themselves more readily to spectroscopic examination, less space is required, the draining of the crystals is more easily accomplished, and there is less danger of contamination from laboratory dust. The loss due to breakage when using flasks was very small and was no greater than when casseroles were used. The dissolving of the crystals was carried out on the water- or steam-bath. At the temperatures attained there was no decomposition unless the solutions became very concentrated, and then only in the more soluble fractions. A series could be fractionated once or twice a day.

According to James and Bissel (*Journ. Am. Chem. Soc.*, 1914, xxxvi., 2060) the order of solubility of the rare earth bromates is as follows, arranged in order of increasing solubility:—Eu (least soluble), Gd, Tb, Dy, Ho, Y, Er, Tm, Yb, Lu, Ct, Sc. The order of increasing solubility of the cerium earth bromates, according to the same authors, is as follows:—Eu, Sa, Nd, Pr, Ce, La. The solubility of neodymium bromate lies between that of gadolinium and terbium.

After about fifty series of crystallisations of the bromates had been carried out, during which time several small fractions had been set aside from the insoluble end, as they

contained, in the main, barium and potassium bromates, the colours of the fractions which were numbered 8 to 31, inclusive, were noted. This, together with a study of the absorption spectra, indicated a composition of the fractions as shown in Table I.

After the series had been fractionated for some time longer it became evident that the terbium collected with the praseodymium, and that ytterbium, lanthanum, and cerium collected in the fractions more soluble than thulium. These observations are in close agreement with those of James and Bissel.

As the separation continued fractions were set aside from both ends of the series from time to time until enough had accumulated to start separate series. Some of the fractions from the soluble end were placed into a series which was being run from the bromates obtained in earlier investigations in this laboratory. New series were started and fractions added to them in such a way as to make the number of earths in a given series as small as possible and to concentrate each earth in a single series. The transfer of a fraction from one series to another was governed by its colour and absorption spectrum. The above method of manipulation may be made more clear by a statement of the composition of some of the series run.

Series A contained mainly yttrium, with erbium at the soluble end and holmium at the insoluble end. The fractions in this series were almost colourless. Concentration of yttrium was sought in this series which contained more material than any of the others.

Series B contained bromates somewhat less soluble than those in series A. It contained mainly yttrium, with some holmium and traces of dysprosium and terbium. It was free from erbium. The fractions were almost colourless. Concentration of yttrium was sought in this series.

Series C contained bromates somewhat less soluble than those in Series B. It contained mainly yttrium, holmium, and dysprosium bromates. It was entirely free from bromates, more soluble than yttrium bromate, but contained small amounts of terbium, praseodymium, and neodymium bromates, which are less soluble than dysprosium bromate. Concentration of holmium was sought in this series.

Series D contained earths of about the same solubility as dysprosium. It consisted mainly of dysprosium, with some holmium and terbium, and traces of praseodymium and neodymium. Concentration of dysprosium was sought in this series.

Series E contained bromates less soluble than those in Series D. It consisted mainly of neodymium and dysprosium, with some praseodymium and terbium. Concentration of terbium and dysprosium was sought in this series.

Series F contained bromates somewhat more soluble than those in Series A. It consisted mainly of yttrium and erbium, with traces of thulium and more soluble bromates. It was entirely free from holmium and less soluble bromates. Concentration of erbium was sought in this series.

Series G contained the most soluble bromates. It contained considerable thulium, ytterbium, cerium, and lanthanum. Concentration of thulium and ytterbium was

sought in this series. The insoluble end fractions gave bluish green solutions and crystallised well, while the soluble end fractions formed colourless solutions and crystallised poorly.

In addition to the study of the absorption spectra of the various fractions, determinations of the average atomic weight aided in following the course of the separations. Two methods of analysis were used for this purpose, the permanganate method of Gibbs (*Am. Chem. Journ.*, 1893, xv., 546) and the sulphuric acid volumetric method. The methods were found to give almost equally satisfactory results for control work. The sulphuric acid volumetric method is much more rapid, though perhaps not of so general application. In this latter method a few tenths of a grm. of the oxide are dissolved in standardised sulphuric acid, approximately tenth-normal. The earth is precipitated from solution by the addition of an excess of approximately half-normal potassium oxalate solution. If the colour of the oxalate is such as to interfere with the indicator colour the oxalate should be filtered off, otherwise this is not necessary. The excess of acid is titrated with standardised sodium hydroxide solution, approximately tenth normal phenolphthalein being used as the indicator. This method is similar in principle to that used by Feit and Przibylla in their atomic weight determinations (*Zeit. Anorg. Chem.*, 1906, l., 249), and is essentially the same as that used by Holden and James in control work (*Journ. Am. Chem. Soc.*, 1914, xxxvi., 638).

Analyses of two samples from separate yttrium earth mixtures, made by two workers in this laboratory, one using the permanganate method, the other using the sulphuric acid volumetric method, gave the results shown in Table II.

TABLE II.

Method used.	Atomic wt. No. 1.	Atomic wt. No. 2.
Permanganate.. . . .	91.85	89.73
Sulphuric acid volumetric	91.52	89.43

A sample from another lot of material gave the value 90.36 by the permanganate method and the value 90.78 by the sulphuric acid volumetric method.

After bromate Series A had been fractionated for about two and one-half years, several thousand crystallisations having been carried out, the fractions richest in yttrium were removed. There was obtained from these over a kilogram. of oxide. The atomic weight according to the permanganate method, as determined by another worker in this laboratory, was 88.94. This was evidently yttrium material of very high purity.

For the conversion of the bromates into oxalates the following method was found most suitable:—To the saturated solution of the bromates is added a concentrated solution of barium chloride. This causes the precipitation of practically all the bromate radical as crystalline barium bromate, and leaves the rare earth chlorides in solution. The solution may be readily filtered and the earths precipitated with oxalic acid, after the addition of free mineral acid to prevent the precipitation of barium oxalate. In this way barium bromate is obtained in suitable condition for conversion of other rare earth material into bromates. Direct addition of oxalic acid to a solution of rare earth bromates should be avoided as it results in the evolution of free bromine and the decomposition of oxalic acid. It is a disagreeable operation as well as a wasteful one.

A sample of earth for analysis was taken from a fraction in a bromate series which had been run for the concentration of erbium for a very long time, until the method seemed to give only very slow further separation. The fraction analysed was judged by its absorption spectrum to be the one richest in erbium and to contain only erbium and yttrium. The atomic weight was found by the permanganate method to be 162.34, which indicated an erbium content of about 93 per cent. Several fractions from this series, of composition very close to that of the sample analysed, were united, and from them were obtained 85

grms. of a very dense rose-coloured oxide. This material was fractionated by sixteen series of fusions by the basic nitrate method. There were thus obtained eight fractions of which the one richest in erbium gave an atomic weight slightly above 164. (This determination was made by another worker in this laboratory and exact data are not available). This value indicated an erbium content of about 95 per cent.

Series C and D, the bromate series which were being run for the concentration of holmium and dysprosium, respectively, proved very interesting. A study of the absorption spectra showed that a rather marked separation had taken place in Series C after it had been fractionated for a long time. Some fifty fractions had been set out of the insoluble end of this series and placed in series containing less soluble bromates. There remained in the series sixteen fractions. A sample from Fraction 54, the least soluble fraction, which contained a large percentage of dysprosium and holmium and small amounts of terbium, praseodymium, and neodymium, was analysed by the sulphuric acid volumetric method. The oxide was cream coloured. The atomic weight found was 161.59. A sample from Fraction 64, which was judged to be richest in holmium, and which contained only traces of dysprosium, together with a large percentage of yttrium, was analysed. The permanganate method gave the value 128.15 and the sulphuric acid volumetric method gave the value 128.28 for the atomic weight. Those values indicated a holmium content of about 50 per cent. A sample from Fraction 69, the most soluble fraction, which showed only holmium absorption, and which gave a cream coloured oxide, was analysed. The sulphuric acid volumetric method gave the atomic weight as 105.22, indicating a holmium content of about 22 per cent.

A study of the fractions of bromate, Series D, after it had been fractionated for a long time in a similar manner to the preceding series, showed that it consisted almost entirely of dysprosium material. There were present small amounts of holmium, terbium, praseodymium, and neodymium. A sample from Fraction 34, the least soluble in the series, which showed slight praseodymium and neodymium absorption bands in addition to those of dysprosium and which gave a light brown oxide, gave the atomic weight 161.19. A sample from Fraction 41 in the same series, which showed holmium absorption bands, but no neodymium, gave the atomic weight 161.92. It was evident from the values obtained, 161.19, 161.92, and 161.59, that the bromates of Series D and those from the insoluble end of Series C were of quite uniform composition. The absorption spectra indicated the presence of but slight amounts of earths other than dysprosium. It was decided to purify further this material for the purpose of securing dysprosium material of sufficient purity for accurate atomic weight determinations and to determine the atomic weight of the element.

To be continued.

The Channel Tunnel and the World War.—This book, copies of which may be had gratuitously, upon application to Mr. R. D. Heckels, Secretary, Channel Tunnel Company, Limited, 84, Tooley Street, London, S.E., contains statements made by many eminent authorities in favour of the construction of a Channel Tunnel. The speeches made at deputations, dinners, meetings, &c., are given verbatim, and opinions both for and against the Tunnel are discussed. A map is provided showing the plan of the Tunnel as proposed in 1913, but the project has been somewhat modified since that date. The great majority of the speeches and articles, both by French and English authorities, are strongly in favour of the plan, and a contribution of particular interest is an article by Lord Sydenham, "The World War: What the Channel Tunnel would have Saved England and Her Allies." In a very striking speech Sir Francis Fox briefly discussed the engineering aspects of the problem, and showed how the difficulties and dangers could easily be met.

THE RARE EARTH COBALTICYANIDE.

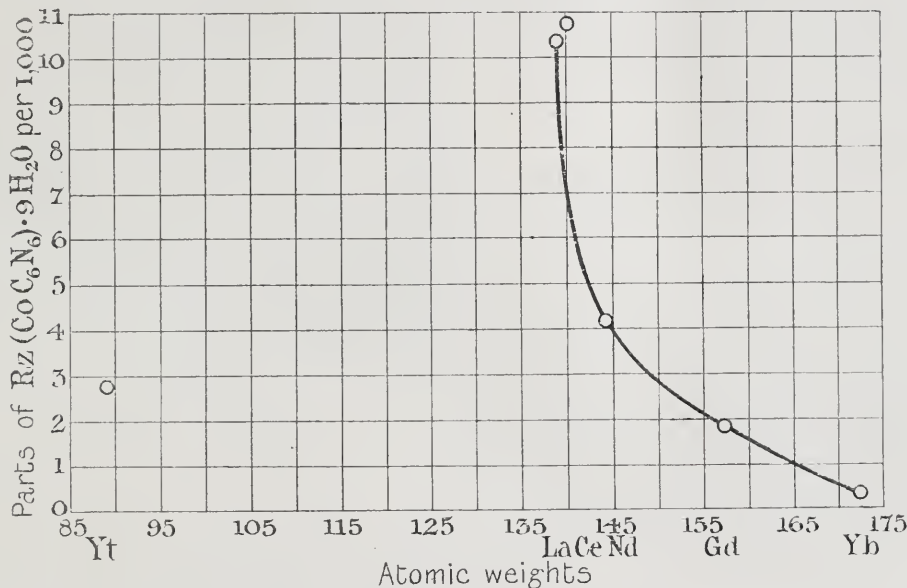
By C. JAMES and P. S. WILLAND.

THE first rare earth cobalticyanide was prepared by Cleve and Höglund (*Bull. Soc. Chim.*, 1873, p. 193). In 1915 the cobalticyanides were examined during a search for a method to separate yttrium from erbium (*Journ. Am. Chem. Soc.*, 1915, xxxvii., 2642), and owing to the facts that the separation of yttrium from erbium was rapid, and that neodymium collected in the most soluble fractions, further investigations were carried out with the following results:—

Neodymium Cobalticyanide, $\text{Nd}_2(\text{CoC}_6\text{N}_6)_2 \cdot 9\text{H}_2\text{O}$.—This compound was easily precipitated from a boiling solution of neodymium chloride by adding ammonium cobalticyanide. Neodymium chloride was kept in excess. The salt, which possessed a pale lilac colour, formed a heavy crystalline powder. Microscopic examination showed that the crystals belong to the hexagonal system. They were

amounted to 22.05 per cent, indicating the presence of nine molecules of water of crystallisation. From this it would seem that the rare earth cobalticyanides possess the type formula $\text{R}_2(\text{CoC}_6\text{N}_6)_2 \cdot 9\text{H}_2\text{O}$.

Other cobalticyanides were prepared in a similar manner to those described above. The lanthanum salt formed a heavy precipitate consisting of hexagonal bipyramids. They were a little more soluble in water than the neodymium compound, and were somewhat soluble in concentrated hydrochloric acid. Cerium cobalticyanide was obtained as a white crystalline precipitate with a slightly yellow tint. The solubility in water and concentrated hydrochloric acid was of about the same degree as the lanthanum salt. Gadolinium cobalticyanide formed very quickly. The precipitate was very finely divided and almost insoluble. Ytterbium cobalticyanide was white, crystalline, and insoluble. When a solution of potassium cobalticyanide was boiled with a solution of thorium nitrate, no precipitate formed, even though the original volume had been greatly reduced.



almost insoluble in water, very slightly soluble in concentrated hydrochloric acid, and rapidly decomposed by boiling sodium hydroxide.

In order to determine the percentage of neodymium, some of the material was boiled with sodium hydroxide to decompose it. The hydroxide, after filtering and washing well, was dissolved in dilute hydrochloric acid and precipitated as the oxalate. This was ignited and weighed. The average for the neodymium amounted to 32.80 per cent, which seemed to indicate that the formula should be $\text{Nd}_2(\text{CoC}_6\text{N}_6)_2 \cdot 9\text{H}_2\text{O}$. The cobalt was determined by electrolysis after breaking up the salt by fusion with bisulphate and rendering the solution alkaline by ammonium hydroxide. The results were a little below the theoretical.

When the compound was heated it gave off water and gradually turned blue. At higher temperatures it underwent rapid decomposition with the evolution of sparks.

Yttrium Cobalticyanide, $\text{Y}_2(\text{CoC}_6\text{N}_6)_2 \cdot 9\text{H}_2\text{O}$.—This salt was prepared by precipitating a boiling solution of yttrium nitrate with a hot solution of potassium cobalticyanide. The precipitate was crystalline and creamy white in colour. It was almost insoluble in water and hydrochloric acid, but was decomposed by boiling with sodium hydroxide.

The percentage of yttrium was determined in a similar manner to that of neodymium. The yttrium found

In order to obtain some comparison of the solubilities of these compounds, they were rotated in a thermostat with 10 per cent hydrochloric acid. Three grms. of each salt were placed in a bottle with 50 cc. of hydrochloric acid having a sp. gr. of 1.050 at 15°. After they had rotated for two weeks at 25° they were allowed to settle. Some of the liquid was weighed, precipitated with oxalic acid, and allowed to stand fifteen hours before filtering, igniting, and weighing. From these results the parts per thousand were calculated and plotted against the atomic weights.

Compound.	Atomic weight.	Parts per thousand.
$\text{La}_2(\text{CoC}_6\text{N}_6)_2 \cdot 9\text{H}_2\text{O}$	139.0	10.41
$\text{Ce}_2(\text{CoC}_6\text{N}_6)_2 \cdot 9\text{H}_2\text{O}$	140.25	10.75
$\text{Nd}_2(\text{CoC}_6\text{N}_6)_2 \cdot 9\text{H}_2\text{O}$	141.3	4.19
$\text{Gd}_2(\text{CoC}_6\text{N}_6)_2 \cdot 9\text{H}_2\text{O}$	157.3	1.86
$\text{Yb}_2(\text{CoC}_6\text{N}_6)_2 \cdot 9\text{H}_2\text{O}$	172.0	0.38
$\text{Y}_2(\text{CoC}_6\text{N}_6)_2 \cdot 9\text{H}_2\text{O}$	89.0	2.78

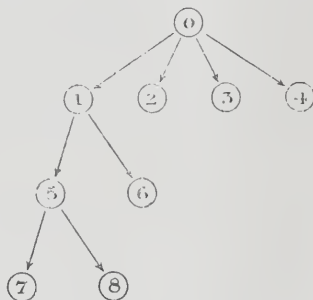
The curve obtained from the above data showed that yttrium cobalticyanide is of about the same solubility as the samarium and europium compounds, and more than three times more soluble than the erbium salt. The separation of yttrium and terbium would seem to be less efficient, since the terbium salt is about twice as soluble as that of erbium.

Separation of Mixed Oxides.

1. *Oxides containing Dysprosium, Holmium, and Yttrium, with Traces of Erbium, Terbium, and Neodymium.*—These were dissolved in nitric acid, diluted to about 600 cc., boiled, and a solution of potassium cobalticyanide added until a quantity of precipitate had formed. This was filtered off and the process repeated. The precipitates were boiled with sodium hydroxide, filtered, washed, and dissolved in nitric acid. The solutions were then precipitated as the oxalates, ignited, and again converted into the nitrates, the solutions of which were examined by means of a spectroscope.

Fraction I. showed very strong holmium and dysprosium bands and traces of neodymium and erbium. In Fraction II. holmium and dysprosium were still very strong, neodymium was weak, and there was a trace of erbium. Fraction III. showed strong neodymium, dysprosium, and holmium bands. There was a slight trace of erbium. In Fraction IV. neodymium was stronger while holmium and dysprosium were weak. The material was mainly yttrium nitrate.

Fraction I. was diluted, boiled, and more cobalticyanide added. The precipitate that formed was filtered off and the remaining rare earth thrown out as the oxalate. These



fractions, V. and VI., were converted to the oxides. V. was again dissolved in nitric acid and split into two more fractions, as shown in the sketch herewith.

In colour the oxides varied from a chocolate brown to a light chamois, proportional to the equivalents, showing that terbium tends to go to the least soluble end. All the oxides were boiled with water to remove any alkali metal before the equivalents were determined.

No. of fraction.	Atomic weight
II.	109.5
III.	95.2
IV.	89.0
VI.	102.3
VII.	132.9
VIII.	122.4

2. *Separation of Erbium from Yttrium.*—The oxide used was very rich in erbium. Twenty-five grms. were dissolved in hydrochloric acid, diluted to about 800 cc., and precipitated as in the case of the dysprosium, holmium, and yttrium oxides. Two fractions were taken, and these, after converting to oxides and re-dissolving, were again fractioned. Fraction I. gave Fractions III., IV., and V., while Fraction II. gave Fraction VI. and VII. The oxides varied from a rose-colour to an extremely pale pink. Fraction III., the least soluble, possessed the most colour, and Fraction VII., the most soluble, was the palest.

No. of fraction	Atomic weight.
III.	142.3
IV.	137.2
V.	127.8
VI.	110.1
VII.	93.7

The cobalticyanide method is excellent for the separation of yttrium from erbium and *vice versa*. The precipitates are very crystalline, and the process can be quickly carried out.

One of the authors and another are investigating the ferricyanides, which are nice crystalline compounds, and which differ very considerably in their solubilities. By fractionally precipitating a solution of the nitrates of yttrium and erbium with potassium ferricyanide, a rapid separation is effected.—*Journal of the American Chemical Society*, xxxviii., No. 8.

PROCEEDINGS OF SOCIETIES.

THE INSTITUTION OF PETROLEUM
TECHNOLOGISTS.

At the Fourth Annual General Meeting of the Institution the following elections were announced:—

President—Mr. Charles Greenway.

Vice-President—Prof. John Cadman.

Honorary Members—Sir Frederick Black, C.B.; M. Jor A. Cooper-Key, C.B.

Vice-Presidents—The Rt. Hon. Viscount Cowdray of Cowdray; Sir Thomas H. Holland, K.C.I.E., D.Sc., F.R.S.; Sir Boverton Redwood, Bart., D.Sc., F.R.S.E.

Council—Alfred C. Adams; Herbert Allen; Sir Robert Balfour, Bart., M.P.; Capt. R. W. Barnett, M.P.; Herbert Barringer, M.Inst.C.E., M.I.Mech.E., M.I.N.A.; Sir George Beilby, LL.D., F.R.S.; Edwin R. Blundstone, B.A., F.C.S.; Andrew Campbell; John T. Cargill; E. H. Cunningham Craig, B.A., F.R.S.E., F.G.S.; Arthur W. Eastlake, M.Inst.M.E., A.M.I.Mech.E.; T. C. Palmer, Assoc.M.Inst.C.E.; F. Mollwo Perkin, Ph.D., F.I.C., F.C.S.; Robert Redwood, F.C.S.

NOTICES OF BOOKS.

One Hundred Chemical Problems. By E. ARTHUR MASON, B.Sc. (Hons.). London: G. Bell and Sons, Ltd. 1917. Pp. 8. Price 6d. net.

THE chemical problems in this pamphlet are classified according to subjects and include numerical questions and calculations on molecular weights, the determination of equivalent and atomic weights, corrections for temperature and pressure, vapour density experiments, diffusion, and some miscellaneous problems. The questions are mostly of a straightforward type and are fairly easy, and the book will be useful for candidates for the University Local and other examinations who require some practice in chemical arithmetic.

Practical Sanitation. By GEORGE REID, M.D., D.P.H. Eighteenth Edition, Revised. London: Charles Griffin and Co., Ltd. 1916. Pp. xii+367. Price 6s. net.

THIS book is known to all sanitary engineers and inspectors, and it is possibly quite unnecessary to call attention to its excellence, for all who are interested in the subject will be fully aware of it. It is undoubtedly the most authoritative and widely used text-book on sanitation in the English language, and is quite without a rival in its own line. The fact that this last edition is the eighteenth, issued twenty-five years after the first, is sufficient proof in itself that the book has been thoroughly appreciated. The last edition has been brought up to date, and some trifling alterations have been made, although the main plan is unaltered. The Appendix on Sanitary Law has been completely revised, and the matters dealt with in it are now included in the general index and are not indexed separately as before.

A Practical Manual of Autogenous Welding (Oxy-acetylene). By R. GRANJON and P. ROSENBERG. Translated by D. RICHARDSON, Wh.Ex., A.M.I.M.E. Fourth Edition. London: Charles Griffin and Co., Ltd. 1916. Pp. xxii+244. Price 5s. net.

The fourth edition of this most useful work has been thoroughly revised and edited by the translator, and additional explanations are given of some parts which were originally a little difficult to follow. Many fresh illustrations have been added, and new information which has been accumulated since the publication of the third edition in 1915. The book is a thoroughly practical guide for the welder, who will be able to learn from it all the details of his art, the best methods of manipulation, and the choice of materials and apparatus.

A Text-book of Thermo-chemistry and Thermodynamics. By Prof. OTTO SACKUR, Ph.D. Translated and Revised by G. E. GIBSON, Ph.D. London: Macmillan and Co., Ltd. 1917. Pp. xvi+439. Price 12s. net.

THE essential facts of thermodynamics which must be thoroughly understood before the student can hope to obtain any real grasp of the principles of physical chemistry are very clearly explained in this book. The translator has made a good many alterations in the text and is responsible for some important additions and new sections. Thus, to mention a few changes, the discussion of the theory of Debye is original, and also the whole of the chapter on thermodynamic equilibrium in general, which takes the place of the section on "Freie Energie und Thermodynamisches Potential" in the German edition. The section on the distribution of energy in the spectrum has been entirely rewritten and is a very successful piece of work. There is much to commend in the book, which provides a very satisfactory course of thermodynamics for the use of the advanced student. The explanations are always concise and clear, and every effort has been made to foresee difficulties and to throw light upon some matters which students frequently find particularly puzzling. Heat radiation and the Nernst heat theorem are very well treated, and the numerical illustrations of important formulæ and the worked out calculations are likely to provide valuable aid in rendering the student's ideas clear and definite.

Year Book of Pharmacy and Transactions of the British Pharmaceutical Conference, 1916. London: J. and A. Churchill. Pp. 572. Price to Non-members, 10s.

THE Year Book of Pharmacy for 1916 contains detailed reports of the Annual British Pharmaceutical Conference held in London in July, at which an interesting Address on the "Drug Resources of India and the Colonies" was delivered by the President, Dr. David Hooper, F.I.C. The Year Book also contains abstracts of papers on scientific subjects published from July, 1915, to June, 1916, in papers and journals in all languages. They are classified under various headings—chemistry, essential oils, materia medica, new remedies, new apparatus, &c.—and are well indexed. A list of subjects suggested for investigation is also given, and the Executive Committee of the British Pharmaceutical Conference hope that work will be undertaken upon them. Some of the subjects have already been appropriated, so that it is advisable that intending researchers should communicate with the Secretary before beginning work. A special fund exists to defray expenses in connection with research work, and applications from members of the Conference for grants will be considered by the Executive Committee.

General Chemistry for Colleges. By ALEXANDER SMITH, Second Edition. London: G. Bell and Sons, Ltd. 1916. Pp. x+662. Price 6s. 6d. net.

THE second edition of this book has been practically rewritten, so that it may be regarded as a new work possessing, however, all the excellent features to which the earlier

edition owed its great success. Although suitable for students of college age and intellectual attainments, those who had no previous knowledge of chemistry would quite well be able to profit by its use, and it is safe to say that any who had studied the subject before would find that it cleared up many difficulties and hazy ideas in an astonishing fashion. Special stress is laid upon the historical and philosophical aspects of the subject, and the student is well trained in clear precise thinking and the careful use of appropriate words. The introduction on "Chemical Views of Matter and Chemical Change and Methods of Studying it," the chapters on Electro-motive Chemistry," and on "Solutions," are particularly striking examples of the author's lucid style, and one great improvement in the second edition is the increased attention paid to theoretical discussions. The questions at the ends of the chapters will be found very helpful, as will also the clear and full descriptions of methods of performing calculations.

CORRESPONDENCE.

COMMERCIAL SUPPLY OF POTASH.

To the Editor of the Chemical News.

SIR—The purpose of the present is to ask you to supply us with the following information:—

We foresee the possibility of exporting potash after the war, as the internal production greatly exceeds the local demand.

1. Is potash used in industrial concerns, and in which branch? The total quantity of potash used yearly, according to quality and destination (the requirements of various branches of industry).

2. Is the requirement of the said article satisfied exclusively by local production; exclusively by imported potash, both by local production and imported? Point out the relative importance on the market of American and Russian potash, mentioning the relation according to the various qualities. Statistics as to quantity of local production and imported potash for the last year, mentioning the quantity for each quality separately, and in the case of imported goods also from which country. Data (for each quality of raw produce, ashes, wood, stalks, sunflowers, and buckwheat, &c.) used in the country, both local production and imported.

3. Prices and fluctuations of same on the local markets for the years 1913—1916, and the present prices according to quality. General remarks as to the local markets (each separately), relative position of demand and offers, tendencies for the decrease or increase of demand, &c., for the above period.

4. Conditions of import (cash c.i.f. or f.o.b. credit, names and addresses of banks specially connected with the import of potash).

5. The comparative position of competition on the local potash market, as well as other potassium salts.

6. Addresses of local producers, importers, and exporters of potash, list of largest firms abroad exporting potash on the local markets.—I am, &c.,

V. SAVITZKY, General Secretary.

Russo-British Chamber of Commerce,
4, Gorochovaia, Petrograd,
March 6/19, 1917.

THE DEVELOPMENT OF MINERAL RESOURCES.

To the Editor of the Chemical News.

SIR,—With reference to Mr. Giles's letter I am in hearty agreement with his suggestion as to deep borings, and carried on as a *State enterprise*. I am sure if some central

authority was established where information which is at present available could be collected, tabulated, and to some extent corroborated, we should then find what hitherto little known valuable deposits of minerals exist in the British Isles. I have myself found cobalt ore associated with the hematite and limestone deposits of the mountains in the neighbourhood of Dyserth, North Wales, and am sure most readers can point to some deposits probably in their own locality containing the rarer metals but at the present time undeveloped owing to lack of individual enterprise.—I am, &c.

H. PROCTER SMITH, F.C.S.

Shotton, Chester, April 14, 1917.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Bulletin de la Société Chimique de France.

Vol. xxi.-xxii., No. 1, 1917.

Method of Formation of 6,6-Dichloro-2,2-azobenzoic Acid.—S. Reich and W. Merki.—The authors have found that when hydrocyanic acid acts upon 6-chloro-2-nitrobenzoic aldehyde, and the cyanhydride obtained is saponified, 6,6-dichloro-2,2-azobenzoic acid is obtained in the form of yellow crystalline needles. This acid behaves curiously when reduced; stannous chloride or hydrogen in presence of palladium transforms it into a substance insoluble in alkalis and acids and having the empirical formulæ $C_{14}H_6O_2N_2Cl_2$.

Total Synthesis of Santene.—Gust. Komppa and S. V. Hintikka.—The authors have already shown that camphenilone can be transformed into isocamphenilone by first reducing it and then acting on the alcohol thus obtained with phosphorus pentachloride. When HCl is removed from the chloride of camphenilyl a hydrocarbon is obtained, namely, camphenilene, and this gives the acetate of isocamphenilyl on treatment with sulphuric acid mixed with acetic acid. On saponification isocamphenilol is formed and isocamphenilone by oxidation. It has now been found that the hydrocarbon is not a single substance, but is a mixture containing santene, while the isocamphenilolol is identical with santenol and the isocamphenilone with santenone.

MISCELLANEOUS.

Co-operation and Research Work.—Recent enterprises in connection with the preparation of food and the development of its concessions in West Africa and elsewhere, have led to the establishment of a Research Department by the Co-operative Wholesale Society, and Dr. Geoffrey Martin, M.Sc. (Bristol), B.Sc. (Lond.), has just been appointed to direct its work. Dr. Martin is a well-known chemist and the author of several standard works on the application of science to industry. This appointment marks a new departure in connection with the co-operative movement, and has been rendered necessary by the concessions acquired by the Co-operative Wholesale Society in West Africa, Nigeria, and elsewhere, as well as by the development of fresh undertakings at home.

Royal Institute of Public Health.—The Institute is accomplishing valuable patriotic and medico-educational services by lectures and discussions on "Public Health Problems Under War and After War Conditions." A

second Course is to be held during the Spring and Summer on Wednesdays, at 4 p.m., in the Lecture Room of the Institute, 37, Russell Square, W.C. 1. The lectures are being delivered by distinguished experts, and each discussion is to be presided over by a well-known public leader. The following condensed version of the programme indicates the representative character of the course:—

April 18.—"Mental States and the War," by Sir Robert Armstrong Jones, M.D., F.R.C.P.

April 25.—"Citizenship and Health Questions in War Time," by Dr. Chas. Porter.

May 2.—"Imperial Health and the Dysgenics of War," by C. W. Saleeby, M.D., F.R.S.Ed.

May 9.—"The Pathology of Venereal Disease," by Major F. W. Mott, M.D., F.R.S., F.R.C.P.

May 16.—"Public Health and the Control of the Liquor Traffic," by The Rt. Hon. Lord D'Abernon.

May 23.—"The Re-education and Training of Disabled Combatants," by Sir C. Arthur Pearson, Bart.

May 30.—"Health and Insect Life in War and Peace," by Dr. A. E. Shipley, F.R.S.

June 6.—"Welfare Work in Factories," by B. Seebohm Rowntree.

June 13.—"The Management of Neurasthenia and Allied Disorders in the Army," by Hon. and Temp. Lt.-Col. Sir John Collie, M.D.

June 20.—"Food Production in Peace and War," by Dr. E. J. Russell, F.R.S.

June 27.—"The Value and Importance of Physical Exercises from a National Standpoint," by Sir William Milligan, M.D.

July 4.—"Civil Sanitation and the War," by Prof. E. W. Hope, M.D., D.Sc.

July 11.—"Feeding a Nation," by Prof. D. Noel Paton, M.D., F.R.S.

July 18.—Lt.-Col. S. Monckton Copeman, M.D., F.R.S., R.A.M.C. (T.F.).

Each Lecture will be followed by a discussion, in which representative men and women will take part. A syllabus of the course may be obtained on application.

MEETINGS FOR THE WEEK.

TUESDAY, 24th.—Royal Institution, 3. "Russian Development—The Rise of Moscow," by Prof. C. R. Beazley.

WEDNESDAY, 25th.—Royal Society of Arts, 4.30. "Flour and Bread," by Sir Francis Fox.

THURSDAY, 26th.—Royal Institution, 3. "Industrial Finance after the War—Its Financial Needs, How they can Best be Met," by Prof. H. S. Foxwell.

FRIDAY, 27th.—Royal Institution, 5.30. "The Organs of Hearing in Relation to War," by J. Dundas Grant.

SATURDAY, 28th.—Royal Institution, 3. "Principles of Aerial Navigation," by Prof. G. H. Bryan.

A TEXT-BOOK OF THERMO-CHEMISTRY AND THERMO-DYNAMICS.

By Professor OTTO SACKUR, Ph.D. Translated and Revised by G. E. GIBSON, Ph.D., Instructor in Chemistry in the University of California. 8vo. 12s. net.

THE ATHENÆUM.—"As a work dealing especially with the relations of thermo-dynamics and physical chemistry, this book should be of considerable value for reference and study."

NEW EDITION JUST PUBLISHED.

THEORETICAL CHEMISTRY FROM THE STANDPOINT OF AVOGADRO'S RULE AND THERMO-DYNAMICS.

By Professor WALTER NERNST, Ph.D. New Edition, Revised by H. T. TIZARD, M.A. 8vo. 15s. net.

MACMILLAN & CO., LTD., LONDON.

THE CHEMICAL NEWS

VOL. CXV., No. 2996.

GRAIN SIZE MEASUREMENTS IN METALS, AND IMPORTANCE OF SUCH INFORMATION.

By ZAY JEFFRIES, B.Sc., Met.E.,
Case School of Applied Science, Cleveland, Ohio, U.S.A.

Of the two general methods for the testing of metals, namely, chemical and physical, the former has probably reached the higher state of perfection. Its value as a testing method and as a means of control of metal for specific uses is unquestioned. However, it is the physical and mechanical properties of metals which most interest the user. A metal is used for a certain purpose for the reason that it has certain properties which are essential for such purpose. Of two metals or alloys having desirable properties for a certain use, the one which can be produced the cheaper will be the more desirable metal or alloy to use from an economic standpoint. Frequently both chemical and physical specifications have to be met by the manufacturer of metals or alloys. Not infrequently the chemical specifications may be fulfilled and yet the physical specifications will be lacking, and, on the other hand, the physical specifications may be fulfilled and the chemical analysis may not be within the prescribed limits. Such a state of affairs has produced a growing tendency toward the elimination of chemical specifications. It is quite common at the present time, especially in America, to specify certain properties, such as tensile strength, per cent, elongation, reduction of area, elastic limit, hardness, resistance to alternating stresses, electrical conductivity, &c., and to give the manufacturer a great degree of freedom as regards chemical composition. While this method might have its dangers, where it does not seem feasible to make both chemical and physical specifications, it is far better to trust to the physical tests than the chemical analysis.

With the chemical composition of a given metal or alloy remaining the same, the physical and mechanical properties may vary greatly, due to changes in structure. Theoretically, in such cases every change in structure should bring about a change in some or all of the physical properties.

By far the greater part of the microscopic work which has been done so far on metals and alloys has been qualitative in its nature. There are thousands of micrographs recorded which have been taken with the idea of demonstrating the qualitative differences. These micrographs represent only a small portion of the actual samples which have been examined. While there is always a tendency to compare the samples quantitatively, such estimations have been made usually by direct visual comparison, either macroscopically or microscopically. In a great many cases, if metallographists would make an attempt to classify specimens, even according to the visual method, the profession would profit greatly by this information.

In metals and alloys consisting principally of one component, namely, commercially pure metals, compounds, or solid solutions, the quantitative estimation of the structure can best be made by determining the grain size. Grain size determinations are of no value unless certain physical or mechanical properties can be ascertained from them. The only way that grain size determinations can be interpreted is to correlate the grain size with the physical properties of the metal or alloy and with its performance in actual use. This is precisely the process by which the tensile, hardness, and torsion tests have reached their

present state of usefulness, and even after thousands of determinations these tests can only be approximately interpreted. It is therefore evident that grain size determinations will be of little commercial value until the proper correlations are made.

The present paper will point out certain cases where grain size measurements might be employed profitably, although, due to the decided lack of actual grain size measurements, it is possible at the present time to interpret only a few of such determinations. The more important methods for the determination of grain size will be briefly outlined with notes regarding their accuracy. A new method for grain size determinations, first used by author (the empirical constants now in use where this method is employed were determined by A. H. Kline and E. B. Zimmer, American Steel Foundries, Alliance, Ohio), which combines accuracy with speed and requires no apparatus which is not found in metallographic laboratories, will be outlined, together with methods for its application (Zay Jeffries, A. H. Kline, and E. B. Zimmer, "The Determination of Grain Size in Metals," *Bull. A.I.M.E.*, December, 1915; also *Iron Age*, February 3, 1916).

Value of Grain Size Determinations.

In the amorphous cement theory, conceived by Beilby and ably championed by Rosenhain, Humphrey, and others, it is considered that all metals or alloys in the solid state consisting of more than one allotrimorphic crystal are physical mixtures of the crystalline and amorphous phases of the components; for example, a pure metal having a fine-grained structure would be considered as a physical mixture of the crystalline and amorphous phases of that metal. The finer the grain the greater will be the quantity of the amorphous phase. The physical properties of the metal should vary with change in the quantity of the phases. The physical properties might not be in direct relation to the quantities of the two phases, since the amorphous phase in annealed metals is in such a position, namely, surrounding the crystalline phase, that a small addition to the amorphous material might make a relatively large difference in certain physical properties. Grain size determinations would seem to offer one of the best available methods for the determination of the relative quantities of the crystalline and amorphous phases.

As a means of interpreting physical or mechanical properties, grain size determinations offer a distinct advantage over some of the other methods now in common use. The tensile, compression, hardness, torsion, and shearing tests, for example, break down the original structure of the metal, and by the mechanism of such destruction an attempt is made to interpret the various strength properties. Grain size determinations, where they can conveniently and accurately be made, are made on the metal in the state in which it is to be used.

It is well known that, other conditions being the same, the finer the grain in a given metal the greater the tensile strength and the elastic limit. The tensile test is by far the most used of any physical test in controlling metals used industrially. (The Brinell hardness test is replacing the tensile test in some places at the present time). However, in most metals the change in grain size is more appreciable than the changes in any of the properties determined by the tensile test. In metals which have been submitted to high temperatures or are coarse grained for any other reason, grain size may prove to be a better indication of the life of the metal in use than the tensile test. This is especially true where vibration is encountered. The author has replaced the tensile test in the control of metal, for a certain use, by grain size determinations, and the latter method seems to be about five times as sensitive as the tensile test in estimating the life of the metal part in use.

W. Rosenhain makes the following statement in his book "Introduction to Physical Metallurgy," in 1914, in considering the properties of coarse grained metals:—

"The question then arises whether the increased size of

* A Paper read before the Faraday Society, May 9, 1916.

crystals produced in a simple metal by prolonged heating is injurious or otherwise, so far as the useful properties, and more especially the mechanical properties, of the metal are concerned. There can be little doubt that within reasonable limits the mechanical properties of a simple metal are better the smaller the constituent crystals of which it is built up. Under the tensile test, coarseness of structure usually results only in a slightly lowered yield-point, while the ultimate stress and the elongation are little impaired, although the reduction of area at fracture is sometimes markedly less. . . . On the other hand, under both shock and fatigue tests, a coarse structure, even in a simple metal, gives unsatisfactory results."

C. H. Mathewson and Arthur Phillips also find that the grain size determination is more sensitive than the tensile test for the estimation of the strength properties in α -brass (Bull. A.I.M.E., January, 1916, 33-39). They find in one instance a difference of about 30 per cent in the number of grains per square inch, and a difference of only 4 per cent in the tensile strength. From this it appears "that with due allowance for errors in counting, this method is more sensitive in detecting variations in strength properties than the tensile tests themselves."

Table I. gives a comparison of the tensile properties, hardness, and grain size between two α -brass samples of the same composition, according to Mathewson and Phillips.

TABLE I.—Summary of Properties after Half-hour Anneal at 550°—Brass containing 66.56 per cent Copper, 0.26 per cent Lead, 0.08 per cent Iron.

Initial reduction (per cent)	20	50
Elongation in 1 inch (per cent)	72	73
Reduction of area (per cent)	59.5	62.0
Ultimate strength (lbs. per square inch)	46,739	47,100
Scleroscope	10	10
Grains per square inch at 85 diameters	55.5	67.0

It is seen from the above that grain size measurements might be employed profitably, especially to supplement the tensile tests.

A decreasing size of grain increases the hardness of a given metal or alloy. A good example of the relation between grain size and hardness is given by Fahrenwald ("A Development of Practical Substitutes for Platinum and its Alloys, with Special Reference to Tungsten and Molybdenum," Bull. A.I.M.E., January, 1916). Pure gold was prepared, having 4° of grain size, varying from extremely fine grained metal prepared from colloidal gold to coarse grained cast gold. The Brinell hardness varied from 23.8 in the coarse grained sample to 94.7 in the fine grained sample. Here, again, we have the quantitative measurements of the hardness, but not of the grain size. The grain size is referred to as coarse grained and fine grained, which are, of course, only relative terms.

It is probable that grain size measurements would throw some light on certain corrosion problems. While it has been reported that in certain cases metals are more resistant to corrosion in the cold-worked than in the annealed state, usually the latter offers the more resistance to corrosion (William E. Gibbs, "Corrosion of a Solid Solution: 70-30 Brass," contribution to a General Discussion on the "Corrosion of Metals," held before the Faraday Society, December 8, 1915). It would seem that, other conditions remaining the same, the greater the quantity of amorphous material present, the greater would be the rate of corrosion. In this connection Leslie Aitchison makes the following statement ("Experiments on the Influence of Composition upon the Corrosion of Steel," contribution to a General Discussion on "The Corrosion of Metals," held before the Faraday Society, December 8, 1915):—"Whichever or whatever explanation be accepted as the cause of this amorphous layer, its presence can hardly be doubted, and its influence upon corrosion cannot be neglected." He also states that twinning in solid solutions may have an influence upon corrosion.

Fine grained metals will volatilise more readily at high temperatures than coarse grained (Rosenhain and Ewin, "Inter-crystalline Cohesion in Metals," Journ. Inst. Metals, 1912, viii.). When metals are to be used at high temperatures, and where volatilisation is a factor in the life or performance of the metal, such as in incandescent lamps and resistance wires for electric furnaces, it can be readily seen that coarse grained material will give less trouble from volatilisation. While fine grained metals are stronger and have higher elastic limits than coarse grained metals at low temperatures, the reverse is true at relatively high temperatures.

In metals which have been cold worked the shape of the grains as determined by microscopic methods offers the best means for the quantitative estimation of the degree of cold work. Where it is possible to get this information from the working conditions, namely, the relative sizes of the metal piece before and after cold working, this should be done. Since the physical and mechanical properties of metals change greatly with the degree of cold work, the determination of the size and shape of the grains will be found valuable when dealing with such metals.

To be continued.)

OBSERVATIONS ON THE RARE EARTHS.*

By EDGAR W. ENGLE† and CLARENCE W. BALKE.

(Concluded from p. 186).

IV. *History of Dysprosium*.—There is but little regarding dysprosium to be found in the literature. In 1886 Lecoq de Boisbaudran announced that he had been able to divide the earth known as holmia into two earths (*Comptes Rendus*, 1886, cii., 1003; *CHEMICAL NEWS*, 1886, liii., 265). He made the separation by fractionating with potassium sulphate and alcohol. He gave the name dysprosium, from a Greek word meaning "difficult to approach," to the earth which gave the following absorption maxima in solution:— $\lambda = 753, 475, 451.5, 427.5$. Boisbaudran (*loc. cit.*) did not succeed in freeing the new earth from terbium.

In 1906 Urbain (*Comptes Rendus*, 1906, cxlii., 785) announced the isolation of about 50 grms. of the dysprosium of Boisbaudran. He studied the absorption in the ultra-violet region, gave the atomic weight as 162.49, and stated that the characteristics of its compounds range it in the rare earth series between terbium and holmium. He found no evidence of the complexity of the element. He recommended the fractionation of the ethyl sulphates and of the simple nitrates as being most suitable for the separation of yttrium and terbium from dysprosium. However, neither of these methods was very satisfactory for the separation of holmium from dysprosium.

In the same year, Urbain and Dementioux published a series of determinations of the atomic weight of dysprosium (*Comptes Rendus*, 1906, cxliii., 598). As a result of twelve determinations, which gave values from 162.29 to 162.75, they give 162.54 as the most probable value for the atomic weight. Their determinations were made by transforming the octohydrated sulphate, $Dy_2(SO_4)_3 \cdot 8H_2O$, into the oxide, Dy_2O_3 , by calcination at white heat. Few details are given. In 1908 Urbain mapped the spark spectrum of dysprosium and determined the magnetic susceptibility of its oxide, Dy_2O_3 (*Comptes Rendus*, 1908, cxlvi., 922). Bourion (*Comptes Rendus*, 1907, cxlv., 243; *Ann. Chim. Phys.*, 1910, [8], ccclxxxi., 21, 77), Urbain and Jantsch (*Comptes Rendus*, 1908, cxlvi., 127), Jantsch and Ohl (*Ber.*, 1911, xlv., 1274) have prepared and studied several compounds of dysprosium. Moseley (*Phil. Mag.*, 1914, xxvii., 703), in his table of the elements, in which the arrangement is based upon the high frequency spectra, gives the atomic number of dysprosium (symbol given as Ds) as 67,

* *Journal of the American Chemical Society*, xxxix., No. 1.

placing it between holmium (66) and erbium (68). Dushman (*Gen. Elec. Rev.*, 1915, xviii., 614) mentions the fact that in Moseley's table the order of atomic numbers in the case of dysprosium and holmium is apparently the reverse of that of the atomic weights.

V. *Fractionation of the Simple Nitrates for the Separation of Dysprosium.*—Fractionation of the bromates showed that the last traces of praseodymium and terbium could be removed from dysprosium but very slowly, if at all, by this method. Accordingly, it was decided to convert the dysprosium rich material from Series D and from the insoluble end of Series C into nitrates and ethyl sulphates, and fractionate these salts. From the least soluble fractions in Series D were obtained 86 grms. of a light brown oxide containing dysprosium, with small amounts of neodymium, praseodymium, and terbium, and a faint trace of holmium. The atomic weight as determined by the sulphuric acid volumetric method was between 161.2 and 161.9. The oxide was dissolved in nitric acid. Bismuth nitrate was added, and the fractional crystallisation carried on in nitric acid solution of about 60 per cent nitric acid. According to Urbain (*Comptes Rendus*, 1909, cxlix., 37), bismuth nitrate is very slightly less soluble than terbium nitrate, dysprosium nitrate is more soluble than terbium nitrate, and neodymium nitrate is more soluble than dysprosium nitrate in nitric acid solution. The nitrates crystallise well and the mother liquors are easily drained off. There is considerable tendency towards the formation of supersaturated solutions unless seeding is resorted to or a slight amount of the solid left undissolved when solution for recrystallisation takes place. This is also true of the bromates. The nitrates were run through about fifty series of crystallisations. As a result of these crystallisations the absorption spectra and the colour of the oxides showed that but slight change was taking place. Neodymium concentrated somewhat at the soluble end (Demarcay, *Comptes Rendus*, 1900, cxxx., 1019). It was decided to change the earth nitrates into ethyl sulphates, since an ethyl sulphate series being fractionated at the same time was found to be giving a good separation. The nitrate fractions were united, with the exception of five fractions at the soluble end, which were set aside as most of the neodymium had concentrated in them. Bismuth was removed from the united fractions by dilution and by precipitation with hydrogen sulphide. The earths were precipitated with oxalic acid. The oxalates obtained were ignited to oxides. The weight of the oxides was between 75 and 80 grms.

VI. *Fractionation of the Ethyl Sulphates for the Separation of Dysprosium.*—The oxides obtained from the simple nitrate series were dissolved in the calculated amount of ethyl sulphuric acid, N.F. = 0.63 (Urbain, *Journ. Chim. Phys.*, 1906, iv., 31). The oxides dissolved quite readily though it was difficult to get them to neutralise the solution completely. As the ethyl sulphates decompose quite readily it was not considered safe to heat very much in order to hasten solution. The neutral solution finally obtained was evaporated under reduced pressure with gentle warming until quite concentrated, after which air was blown over the surface until solution was evaporated sufficiently for crystallisation. This series was fractionated, using absolute alcohol as a solvent. It was hoped that this would prevent hydrolysis of the ethyl sulphates, which takes place readily in aqueous solution, especially if there is present a trace of free acid (*loc. cit.*). The ethyl sulphates were found to be quite stable under the conditions of fractionation. Care was taken not to heat the fractions any hotter than was necessary to dissolve the crystals. This dissolving was done on a steam-bath kept at a temperature no hotter than the hand could bear with comfort. The ethyl sulphates did not form supersaturated solutions as did the bromates and nitrates. This adds much to the convenience of the fractionation. The slight amounts of neodymium and praseodymium present in the series concentrated rapidly in the least soluble fractions. The terbium concentrated in the less soluble fractions also, but

not nearly so rapidly as did the neodymium and praseodymium. The dysprosium, with the slight trace of holmium present, concentrated in the middle and most soluble fractions. This series will be referred to later as the first ethyl sulphate series.

The bromates from the more soluble fractions of Series D, having an atomic weight of 161.6 to 161.9 as determined by the sulphuric acid volumetric method, were converted to the oxides. The yield was 73 grms. of buff coloured oxide. This was mainly dysprosium, with 1 or 2 per cent of holmium and slight amounts of praseodymium and terbium, and a trace of neodymium. From the method used in fractionating the bromates and from the small percentage of holmium present, it was regarded that this material was free from yttrium, though there was no positive direct evidence of this. The oxide was converted into ethyl sulphate in the manner recommended by James (*loc. cit.*). The procedure was as follows:—The oxide was dissolved in hydrochloric acid to neutral solution. This solution was concentrated and treated with an alcoholic solution of sodium ethyl sulphate. The precipitated sodium chloride was filtered off, and the series was fractionated similarly to the preceding one. This method of preparing the ethyl sulphate was not nearly so satisfactory as that of dissolving the oxide in ethyl sulphuric acid. Considerable sodium salts remained in solution, and were troublesome to remove in the final purification of the material for analysis. As the fractionation progressed the neodymium and praseodymium rapidly concentrated in the least soluble fractions, which were removed from the series from time to time. After the series had been run about twenty times a sample from the soluble end was analysed. The oxide was cream coloured. Check analyses by the sulphuric acid volumetric method gave the values 162.62 and 162.41 for the atomic weight. A sample from an insoluble end fraction gave the value 163.01 by the same method. This series will be referred to later as the second ethyl sulphate series.

Since it appeared that, with the material at hand, dysprosium might readily be isolated with no impurity other than a small amount of holmium, which was not sufficient to affect the atomic weight more than one or two points in the second decimal place, and for which a correction might be made, based on the intensity of the absorption spectrum, it was decided to attempt to determine accurately the atomic weight of dysprosium. With this end in view the fractionation of the ethyl sulphates was continued. It was decided to study the ratio $\text{Dy}_2\text{O}_3 : 2\text{DyCl}_3$ by a method similar to that used for the determination of the atomic weight of yttrium by Egan and Balke (*loc. cit.*).

VII. *Preparation of Reagents used in the Atomic Weight Determinations.*—*Water.*—The ordinary distilled water was redistilled after the addition of alkaline potassium permanganate from the still used in this laboratory for conductivity water.

Oxalic Acid.—Chemically pure oxalic acid was dissolved in hot water. The slight insoluble residue was filtered off, and the acid crystallised twice from dilute nitric acid and twice from conductivity water. After each crystallisation was sucked dry on a Büchner funnel.

Nitric Acid.—Chemically pure nitric acid was distilled from a quartz container, through a quartz condenser into a quartz receiver. The middle third was reserved for use.

Hydrochloric Acid Solution.—This was prepared by heating the concentrated chemically pure hydrochloric acid and passing the gas into conductivity water. Quartz vessels were used throughout.

Hydrogen Chloride Gas.—This was prepared by dropping chemically pure concentrated sulphuric acid on chemically pure concentrated hydrochloric acid. It was dried by passage through two vertical drying towers, each 1 metre high and 2½ cm. in diameter. The towers were filled with solid glass beads wet with chemically pure concentrated sulphuric acid. The entire apparatus was of glass and was continuous.

Ammonia.—This was made as used by warming the chemically pure concentrated aqueous solution.

Nitrogen.—Air was mixed with ammonia and passed through a quartz tube containing copper gauze heated to redness, then bubbled through dilute sulphuric acid. The nitrogen thus obtained was purified and dried as follows:—The gas was passed through a tower 60 cm. high, 2½ cm. in diameter, containing solid glass beads moistened with dilute sulphuric acid, next through a similar tower in which the beads were moistened with chemically pure concentrated sulphuric acid, next through a tower 75 cm. high, 3 and eight-tenths cm. in diameter, loosely packed with solid potassium hydroxide, next through a sulphuric acid tower similar to the preceding one, and finally through a tube 40 cm. high, 2 cm. in diameter, containing glass-wool interspersed with phosphorus pentoxide which had been redistilled directly into the tube. The gas was passed upward through each tower. The purifying and drying train was constructed entirely of glass and was continuous.

Air.—Air was purified and dried in the same way as nitrogen.

The hydrogen chloride, nitrogen, and air trains were all mounted compactly on a wooden support.

Vessels of platinum, quartz, or Jena resistance glass were used in all cases where the use of less resistant containers would have been likely to contaminate the material.

VIII. Preparation of Dysprosium Oxide.—The material for analysis was converted from the ethyl sulphate into the oxide as follows:—The alcoholic solution was diluted with water, a little dilute sulphuric acid added, the solution heated to boiling, and filtered. The object of adding the sulphuric acid was to precipitate any barium which might have been in solution. In the preparation of ethyl sulphuric acid, barium carbonate had been added to remove sulphuric acid. A slight amount of barium ethyl sulphate, which is soluble, was formed here. The dysprosium material was obtained and purified by alternate precipitations with ammonia and oxalic acid, the last precipitation in every case being as oxalate. The precipitation with ammonia was carried out by passing ammonia gas into the hot solution diluted to from 1 to 1½ litres until all the dysprosium was precipitated. The hydroxide was filtered with suction, washed, and dissolved in considerable excess of nitric acid, the solution diluted to from 1 to 1½ litres, heated to boiling, and an excess of a hot solution of oxalic acid added. This was allowed to stand until cool, after which it was filtered and washed with hot water. Precipitated in this way the oxalate filtered readily and was easily washed. The oxalate was then dried, ignited in an electric furnace in platinum, and the oxide dissolved in nitric acid if another precipitation was desired. Each sample analysed was precipitated two or more times with ammonia and two or more times with oxalic acid in the manner described. In addition Sample No. 3 was precipitated with ammonium sebacate (Whitemore and James, *Journ. Am. Chem. Soc.*, 1912, xxxiv., 772; 1913, xxxv., 127). The oxalate finally obtained was ignited for several hours in a platinum crucible to bright redness in an electric resistance furnace. The oxide was then used for the atomic weight determination.

IX. Ratio of Dysprosium Oxide to Dysprosium Chloride.—The above ratio was obtained by converting a weighed amount of the oxide to the anhydrous chloride and determining its weight. The method of procedure was quite similar to that used by Egan and Balke (*loc. cit.*) in their study of a similar ratio for yttrium. The oxide while still hot was transferred to the weighed quartz reaction flask. The bulb of the flask used in this work had a capacity of 25 cc. After addition of the oxide the caps were adjusted over the inlet and outlet tubes, and the flask placed in a desiccator to cool over solid sodium hydroxide. After having cooled one of the joints was loosened for an instant in order to allow the pressure to equalise. The flask was then hung in the balance case for several hours, after which it was weighed. The oxide was then dissolved by the addition of a slight excess of hydrochloric acid with

gentle warming. The solution took place slowly and quietly and without spattering. The flask was next attached to the gas train by means of ground glass joints. The gas train was so arranged that either air, nitrogen, hydrogen chloride, a mixture of air and hydrogen chloride, or a mixture of nitrogen and hydrogen chloride could be passed through the flask at will. Air was first passed in while the solution was heated in an electric oven to 100–105°. When the solution had become quite concentrated the air current was stopped, and a current of hydrogen chloride passed in while the solution was allowed to cool somewhat. Dysprosium chloride separated from the strong hydrochloric acid solution in a well-crystallised form. Air was again passed in and the temperature gradually raised. At this stage care had to be taken in the heating of the flask and in the regulation of the gas current in order to prevent, on the one hand, the solution of the chloride, and, on the other, the formation of an almost impermeable crust of chloride on top of the solution. In order to prevent this latter the entering gas was preheated by passage through a coil of glass tubing enclosed in the oven, and the solution was heated from above by means of a suitable heating coil. When the temperature reached 110° the air current was replaced by nitrogen, and when it had reached 120° hydrogen chloride was mixed with the nitrogen. This was done in order to eliminate the danger of formation of basic chloride. The temperature was allowed to rise to 125°, where most of the water of crystallisation came off. The temperature was allowed to remain at 125° until water ceased coming off, after which it was raised to 200°. Between 125° and 200° no water was given off. Nitrogen was replaced entirely by hydrochloric acid gas when the temperature reached 200°. At 200° water began coming off again, and this temperature was held until most of the water was expelled. A small resistance furnace with alundum core was now placed around the bulb of the flask, the temperature raised slowly to 350°, and kept there for about one and one-half hours after all visible water had been expelled. The furnace was then allowed to come to dull red for a few minutes. It was then removed. A protecting shield of asbestos was placed just above the bulb of the flask to prevent undue heating of the neck during fusion. The current of hydrogen chloride was stopped and the chloride fused with the flame of a Bunsen burner. According to Bourion (*loc. cit.*) the chloride fuses at 680°. As soon as fusion had taken place the flame was removed, and as the flask cooled the hydrogen chloride was replaced by nitrogen, which in turn was replaced by air. While the flask was at room temperature, and while the air was yet passing, the cap was adjusted on the outlet tube. This caused a slight back pressure in the flask which prevented moist air entering the flask while the cap was being quickly adjusted on the inlet tube. The time required for converting a sample of oxide into anhydrous chloride was twenty-five to thirty hours. The flask was hung in the balance case for several hours and weighed.

Dysprosium chloride prepared in the manner just described formed a crystalline olive-green mass which did not wet the flask. There was no indication of volatilisation during the fusion period. The chloride dissolves slowly and completely in cold water to a clear solution, with evolution of considerable heat. The solution is almost neutral to litmus. There is perhaps a faint trace of acidity. The solution obtained in analyses No. 2 was tested with several indicators with the following results:—Blue litmus-paper was changed to red-violet. Red litmus-paper was unchanged. The solution was neutral to methyl-orange, acid to methyl-red, and acid to phenolphthalein. This slight acidity was probably due to hydrolysis, as dysprosium is a relatively weak base in the rare earth series (Urbain, *Comptes Rendus*, 1906, cxliii., 598).

Five consecutive determinations have been made. Samples 1 and 2 were obtained from two fractions near the middle of the second ethyl sulphate series after it had been

run about sixty-five times. These fractions were united and the oxide obtained as previously described. The two samples had the same treatment, with the exception that the oxide of Sample 2 had been ignited eight hours longer than that of Sample 1. The magnetic susceptibility of the oxide from these two samples was determined by Mr. O. A. Randolph, of the Physics Department of the University of Illinois, whom the authors wish to thank for this work. Determinations were made on two portions of oxide. The values obtained for $N_{10^{-6}}$ per unit mass were 291.1 at 24° and 290.6 at 23°. Urbain (*loc. cit.*) gives the value for dysprosium oxide as 290. He does not state the temperature.

Sample 3 was taken from near the middle of the second ethyl sulphate series after it had been run about sixty times. A test of the purity of this sample was made by passing hydrogen sulphide for one-half hour into the aqueous solution of the chloride obtained at the end of the determination. No precipitate was formed, and the solution remained clear. A comparison of the absorption spectrum of the nitrate solution of this sample with a nitrate solution containing a known amount of holmium from a holmium-yttrium mixture indicated the presence of approximately 1.5 per cent of holmium. Assuming the correct atomic weight of holmium as 163.5, the value given in the International Table, this amount would affect the atomic weight of the sample approximately 0.01 unit. The oxides of Samples 1, 2, and 3 had a light cream colour, almost white.

Sample 4 was obtained from the three most soluble fractions in the first ethyl sulphate series after it had undergone about forty series of crystallisations. There was only a very slight trace of holmium in this material. The colour of the oxide was darker than that of the other samples. This indicated the presence of a slight amount of terbium, which seemed to lower the atomic weight.

Sample 5 was obtained from near the insoluble end of the second ethyl sulphate series after about seventy series of crystallisations. The oxide was cream coloured.

All weighings were made by the method of substitution, the tare flask being of quartz, and similar in size, shape, and weight to the reaction flask. The weighings were made on a Ruprecht balance, which is used exclusively for atomic weight work. The weights were carefully standardised to 0.01 mgrm. All weights were corrected to vacuum standard. The specific gravity of the weights was taken as 8.4, that of the chloride as 3.67 (Bourion, *loc. cit.*), and that of the oxide as 7.81, which was determined. The atomic weight of oxygen was taken as 16, and that of chlorine as 35.46. The values obtained are given in Table III.

TABLE III.

Sample.	Wt. oxide. (Grms.).	Wt. chloride. Grms.	Oxide : chloride.	Atomic wt.
1.	0.50906	0.73300	1 : 1.437367	164.354
2.	1.05741	1.51988	1 : 1.437361	164.357
3.	0.65617	0.94352	1 : 1.437920	164.116
4.	1.22603	1.76297	1 : 1.437950	164.104
5.	1.96935	2.83135	1 : 1.437707	164.207

Mean 164.228

X. *Specific Gravity of Dysprosium Oxide.*—In order to change the weight of dysprosium oxide in air to vacuum standard it was necessary to know the specific gravity of this substance. A single determination was made, using oxide from analyses Nos. 1 and 2 of the atomic weight determinations. A Gay-Lussac specific gravity bottle of about 6 cc. capacity was used with water as the liquid. For the weighings in which there was water in the specific gravity bottle this was put inside a weighing bottle to guard against evaporation. Tare vessels similar in size and shape to the containing bottles were used in weighing. Weights were corrected to vacuum standard. Data and results are given in Table IV.

TABLE IV.

Weight of oxide (grms.)	1.4645
Weight of water displaced (grm.)	0.1869
Volume of water displaced (cc.)	0.1875
Temperature	27°
Specific gravity of dysprosium oxide, Dy_2O_3	7.81 27°/4°

XI. Summary of Results.

1. The bromate method of separating the rare earths of the yttrium group has been studied. It has been found sufficient for concentrating erbium, yttrium, and dysprosium material.

2. A comparative study has been made of the permanganate and sulphuric acid volumetric methods for control analyses. They have been found to give practically the same results in earth mixtures whose bromates have a solubility near that of yttrium bromate.

3. Dysprosium material of very high purity has been obtained by fractional crystallisation of the rare earth bromates, followed by fractional crystallisation of the ethyl sulphates.

4. The ratio of dysprosium oxide to dysprosium chloride has been studied, and as a means of five consecutive determinations the value 164.228 obtained for the atomic weight of dysprosium. This value is considerably higher than the one now in the International Table.

5. Some properties of dysprosium chloride are given.

6. The specific gravity of dysprosium oxide was found to be 7.81.

EXPERIMENTS UPON STARCH AS SUBSTRATE FOR ENZYME ACTION.*

By H. C. SHERMAN and J. C. BAKER.

(Concluded from p. 196).

Action of Malt Amylase.—Parallel tests upon the α - and β -amylase substrates at 0.5 per cent concentration were made with a freshly-prepared malt amylase preparation of a diastatic power of 957 (expressed on the scale used since 1910—Sherman, Kendall, and Clark, *Journ. Am. Chem. Soc.*, xxxii., 1973), prepared essentially as described in previous papers from the New York Laboratory of Food Chemistry, but precipitated at a concentration of alcohol slightly higher than usual, viz., 65 to 70 per cent; and also with a preparation purified in the usual way and in which the final active precipitate was obtained at a somewhat lower concentration of alcohol, i.e., Preparation 151, precipitated at 57.5 to 65 per cent alcohol, diastatic power 1240. Except for the kind and amount of enzyme used, the experiments were in all respects similar to those with pancreatic amylase just described. The results with these two malt amylase preparations are given in Tables IV. and V. respectively.

TABLE IV.—Hydrolysis of α - and β -Fractions of Starch by Malt Amylase Precipitated at 65 to 70 per Cent Alcohol.

Time.	α -Amylase substrate.		β -Amylase substrate.	
	Maltose in terms of theory.		Maltose in terms of theory.	
	Per cent.	$k \times 10^3$.	Per cent.	$k \times 10^3$.
30 minutes	10.2	156	5.6	84
60 "	19.2	154	10.8	82
90 "	26.4	148	15.5	81
120 "	32.2	141	22.1	90
150 "	36.7	131	27.4	93
180 "	40.3	124	32.5	95
210 "	43.2	117	36.4	94
240 "	45.8	110	39.8	92
6 hours	50.4	84	53.2	91
24 "	58.1	26	82.2	52

* From the *Journal of the American Chemical Society*, xxxviii., No. 9.

TABLE V.—Hydrolysis of different Substrates by Malt Amylase Preparation 151, Power 1240,

Time.	Soluble starch.		Autoclaved starch.		α -Amylose substrate.		β -Amylose substrate.	
	Maltose in terms of theory.	$k \times 10^3$.	Maltose in terms of theory.	$k \times 10^3$.	Maltose in terms of theory.	$k \times 10^3$.	Maltose in terms of theory.	$k \times 10^3$.
	Per cent.		Per cent.		Per cent.		Per cent.	
30 minutes	29.2	499	26.6	448	28.3	482	19.8	321
60 "	48.4	477	44.0	418	46.8	462	38.8	355
90 "	58.5	424	54.9	384	53.6	401	56.3	399
120 "	62.2	352	59.8	330	57.9	313	70.0	436
150 "	64.3	298	63.6	292	60.3	267	81.8	493
180 "	65.2	255	65.8	258	61.6	231	91.3	590
210 "	66.5	225	67.7	234	62.4	202	97.6	766
240 "	68.2	208	69.5	216	62.7	179	98.7	785
270 "	68.7	188	70.1	198	63.1	162	99.0	748

TABLE VII.—Hydrolysis of different Substrates by Amylase of *Aspergillus oryzae* (Preparation 22b).

30 minutes	10.5	161	11.9	183	12.2	188	4.13	224
60 "	19.8	159	23.0	189	23.4	193	28.5	243
90 "	29.8	171	32.7	191	33.3	195	41.3	257
120 "	35.1	156	39.0	179	39.5	182	51.4	261
150 "	40.0	148	45.7	176	43.4	165	58.9	258
180 "	43.8	139	49.7	167	47.5	155	64.1	247
210 "	46.7	130	53.6	159	50.4	145	67.7	234
240 "	48.8	120	55.6	147	53.2	138	70.0	218
360 "	53.5	92	63.1	121	59.4	108	75.0	168
24 hours	62.8	29	75.4	42	—	—	—	—

Comparison of the data of Tables IV. and V. shows that the purified malt amylase preparations exert in the earlier stages of the digestions a greater saccharifying action upon the α -amylose than upon the β -amylose substrate, while in the later stages the β -amylose shows the greater yield of maltose.

The notable feature of the action of malt amylase upon the β -amylose substrate is the striking way in which the speed of formation of maltose is maintained as compared either with the action of this enzyme upon other substrates or the action of other amylases upon this substrate. In the experiment with a small amount of enzyme (Table IV.) the values of k show no decrease until the formation of maltose is nearly complete, and with a larger amount of enzyme (Table V.) the values of k increase, the time curve being substantially linear, up to a nearly theoretical yield of maltose. This may be expressed as a maintenance throughout the process of the linear relationship usually noted in the earlier stages of such hydrolytic enzyme actions. The explanation is probably to be found in accumulation of hydrolysable products and the efficiency with which the enzyme catalyses the later of the series of consecutive hydrolyses by which maltose is produced. Simultaneous effective catalysis of the successive steps in the process would naturally tend to increase the value of k as computed from the simple unimolecular reaction formula, and this tendency will be further augmented by the fact that the velocity of the reaction during the later stages is compared with that shown at the beginning of the process, where in the case of this enzyme the β -amylose is hydrolyzed less readily than are the other substrates. With the small amount of enzyme used in the experiments of Table IV. this tendency toward a rise in the value of k suffices merely to balance the factors which tend toward a loss or inactivation of the enzyme; whereas with the larger concentration of enzyme in the experiments of Table V. the latter factors are not appreciable, and the rise in value of k becomes very pronounced. Thus the detailed study of the course of the hydrolysis under the influence of a precipitated malt amylase of this character brings out a new difference in behaviour between the α - and β -fractions of the starch.

In all cases the saccharification of the substrate had proceeded to a much higher yield of maltose from β -amylose than from α -amylose when the concentration of enzyme was such as would be used in determinations of

diastatic power and the experiments were sufficiently prolonged to produce maltose up to or beyond half the theoretical yield.

When the amount of enzyme used is much larger the same result may be obtained in a short time, as shown in Table VI.

TABLE VI.—Hydrolysis of α - and β -Substrates with a Relatively Large Amount of Purified Malt Amylase (Preparation 153).

Time.	Reducing sugar as percentage of theoretical yield of maltose.	
	From α -amylose substrate	From β -amylose substrate
20 minutes	54.5	72.4
40 "	67.1	100.0
60 "	68.7	100.2
154 "	71.4	100.8

Evidently even a relatively large amount of enzyme does not readily hydrolyse the material which remains in the α -amylose fraction after two-thirds of the theoretical amount of maltose has been produced, while in the β -amylose fraction under the influence of the same amount of enzyme the hydrolysis runs rapidly to a theoretical yield of maltose. It thus appears that the "resistant dextrin" emphasised by many previous investigators as a product of the action of malt amylase upon starch is derived only from the α -amylose and not from the β -amylose fraction. After the theoretical yield of maltose from β -amylose has been obtained, the increase in reducing power is exceedingly slow, indicating that even this amount of purified malt amylase has only a slight hydrolytic action upon maltose.

The rapid digestion of β -amylose in this experiment explains the statement of Maquenne and Roux (*Comptes Rendus*, 1905, cxi., 1303) to the effect that " α -amylose" (β -amylose) is immediately hydrolysed to the theoretical amount of maltose by malt, since in their experiments very liberal amounts of malt extract were used.

Action of the Amylase of *Aspergillus oryzae*.—Experiments upon Lintner soluble starch, autoclaved whole starch, and α - and β -amylose substrates, all at 0.5 per cent concentration, have been carried out as described above with the amylase of *Aspergillus oryzae* prepared in this laboratory by Dr. A. P. Tanberg from taka-diastase by the purification method described elsewhere (Sherman and Tanberg, *Journ. Am. Chem. Soc.*, 1916, xxxviii.,

1638). The preparation here used was No. 22b, having a diastatic power of 502, as expressed on the scale in use in this laboratory. This corresponds to a Lintner value of about 750. The Wohlgemuth value of this preparation was about 1,000,000.

The results obtained with this amylase preparation are shown in Table VII.

From the data given in Table VII., together with the results of two other series not reproduced here, it may be concluded that the purified amylase of *Aspergillus oryzae* exerts essentially the same saccharogenic action upon Lintner soluble starch, autoclaved whole starch, and the α -amylase substrate, while upon the β -amylase substrate it shows a greater saccharogenic action at whatever stage in the digestion the results be compared. The speed of hydrolysis was not so well sustained in this case as with the other amylases; even in the case of the β -amylase substrate there is here a falling off of the rate of saccharogenic action before the reducing sugar reaches the equivalent of 70 per cent of a theoretical yield of maltose, notwithstanding the fact that this amylase is more active in hydrolysing maltose to glucose than is either pancreatic or malt amylase. This property is doubtless related to the high ratio of amylolytic to saccharogenic activity of this enzyme, which will be considered in the next section.

Relation of Amylolytic to Saccharogenic Action.—In many of the experiments comparing the different substrates the time of disappearance of the blue or violet reaction with iodine was noted, and the amount of maltose which had been formed at this time was found either by direct determination or by interpolation from the determinations of reducing power made at known intervals in the course of the same experiment. While no great accuracy is to be expected of such attempts to determine the stage of digestion at which the starch disappears, as judged by the iodine test, yet they permit comparisons of the amylolytic and saccharogenic activities which at least are not open to such gross discrepancies as may arise when comparisons are made between saccharogenic powers as ordinarily determined and amylolytic powers as determined by the Wohlgemuth method. (For a discussion of these discrepancies see Sherman and Schlesinger, *Journ. Am. Chem. Soc.*, xxxv., 1784).

In the case of pancreatic amylase the present experiments show with each of the four substrates a maltose production from 35 to 50 per cent of the theoretical at the point of disappearance of the blue or violet colour reaction with iodine. Allowing for the difference in experimental conditions, this may be considered as a confirmation for all four substrates of the ratio of about 2 to 1 previously established for the action of pancreatic amylase upon Lintner soluble starch.

In the experiments with the amylase of *Aspergillus oryzae* the iodine end-point occurred at a much earlier stage in the saccharogenic action, usually when from 20 to 30 per cent of the theoretical yield of maltose had been produced. This high ratio of amylolytic to saccharogenic activity and the relatively early decrease in velocity of maltose formation noted above are both indications that this amylase exerts a more pronounced catalytic effect upon the earlier than upon the later of the hydrolyses involved in the transformation of starch through dextrins into maltose.

Malt amylase, on the other hand, is, as shown by the data of Tables IV. and V., an active catalyst of sugar production even in the relatively advanced stages of the process; and apparently it does not correspondingly catalyse the complete disruption of the material to which the iodine test is due, since the iodine end-point is found only at a much more advanced stage of sugar production with this than with either of the other amylases. When acting upon Lintner soluble starch, autoclaved whole starch, or the α -amylase substrate, the malt amylase preparations caused disappearance of the iodine test only when from 65 to 80 per cent of the theoretical yield of maltose had been produced; and when acting upon the β -amylase substrate,

only when the maltose production had reached 85 to 95 per cent. Thus the "delayed iodine end-point" remarked in previous papers as characteristic of the hydrolyses induced by purified malt amylase, is found to be a noteworthy feature of its action upon both α - and β -amylase.

Summary.

Dispersions of commercial potato starch in water or of purified potato starch in water containing a small amount of electrolyte (sodium chloride) have been separated by centrifugal force into a heavier, very viscous, opalescent layer containing the more abundant less soluble component of the starch (Meyer's α -amylase, Maquenne's amylopectin), and a lighter limpid solution containing the less abundant more soluble component (Meyer's β -amylase, Maquenne's amylose).

In designating these two chief components (or derivatives) of starch the terminology of Meyer is preferred to that of Maquenne, not only on grounds of priority, but also as being much more appropriate in view of our present knowledge of the relative abundance of the two components, their properties as compared with the typical properties of starch, and their behaviour toward the amylases.

The centrifugal method here described does not completely separate either component from the other, but affords a means of approximate separation in which the danger of contamination, denaturation, or retrogradation is minimised, and which is well adapted to the study of the effects of the different amylases.

Pancreatic amylase, both in commercial and in highly purified form, produced reducing sugar more rapidly from β -amylase than from α -amylase, autoclaved starch, or Lintner soluble starch, the last three giving very similar results when used as substrate for this enzyme. Not only does the β -amylase substrate show larger yields of maltose at each of the various time intervals tested, but the initial speed of hydrolysis is better maintained with this substrate than with either of the others.

Purified malt amylase shows in the earlier stages of its action a somewhat greater yield of maltose from α than from β -amylase. As the digestion proceeds, the saccharogenic action of this enzyme upon α -amylase becomes slower, while its action upon β -amylase is well sustained, so that in cases in which the hydrolysis proceeds to the production of more than half the theoretical yield of maltose, the final result shows a greater saccharogenic action upon β - than upon α -amylase. The results obtained upon autoclaved starch and Lintner soluble starch are very similar to those found with α -amylase.

The amylase of *Aspergillus oryzae* digests Lintner soluble starch, autoclaved whole starch, and α -amylase at about equal rates, and β -amylase at a somewhat higher rate. Its action upon the β -amylase substrate is, however, not so well sustained as that of pancreatic or malt amylase. This relatively early falling off in the speed of sugar formation, together with the high ratio of amylolytic to saccharogenic power, indicate that this amylase is a more active catalyst of the earlier than of the later stages of the hydrolysis.

Contrasting the action of comparable amounts of the three different amylases, it appears that they catalyse the successive stages of the hydrolysis of β -amylase and its products at relatively different velocities. The time curve for pancreatic amylase is practically logarithmic up to the production of about three-fourths of the theoretical amount of maltose, while beyond this point the reaction proceeds at a lower velocity. Compared with this result, the catalytic effect of the amylase of *Aspergillus oryzae* is more pronounced in the earlier and less pronounced in the later stages, while purified malt amylase is relatively less efficient in the earlier stages but catalyses the later stages more efficiently.

In the digestion of α -amylase all of the amylases showed more pronounced catalytic effect upon the earlier than upon the later stages of the digestion. Starch pastes made at low temperatures (65–80°), autoclaved starch,

and Lintner soluble starch all resemble the α -amylase rather than the β -amylase substrate in their behaviour toward all three amylases, doubtless because α -amylase is the chief component of all these forms of starch.

The separation of starch into its α - and β -fractions made possible a more satisfactory study of the course of the amylase hydrolyses because of the greater homogeneity of the new substrates. All the data pertaining to the earlier stages of these hydrolyses indicate that Lintner soluble starch is well adapted to its purpose as substrate for testing the activities of the different amylases, and that its use leads to conservative estimates of the diastatic powers of purified preparations.

Tested upon any of the four substrates here studied, the three amylases show distinctly different ratios of amylolytic to saccharogenic powers.

BREAD AND FOOD REFORM LEAGUE.*

COMMENT ON A STATEMENT ABOUT THE DIGESTIBILITY OF 80 PER CENT FLOUR.

THE world-wide shortage of wheat makes the full utilisation of this precious food of the utmost importance. It is therefore greatly to be regretted that the Committee appointed by the Royal Society should on inadequate evidence have made the following statement in their Report on the Food Supply of the United Kingdom:—

80 per cent of flour has been shown to make wholesome and palatable bread. Such bread, however, is considerably less digestible than bread made from 70 per cent flour.

This statement is based on American digestibility experiments on the so-called "Entire Wheat Flour," and on other experiments carried out at Cambridge. The 80 per cent flour advocated by the Bread and Food Reform League is not the same thing as the entire wheat flour, which U.S.A. *Bull.* 156 states contains 86 per cent of the wheat grain, and which U.S.A. *Bull.* 126 mentions has only a small amount of the bran removed, and that the latter is like Graham flour, only more finely-ground. Its microphotograph shows that it is not ground to the uniform fineness recommended by the League, and so the gastric juices cannot act so readily on all its particles.

The flour used at Cambridge was also not comparable to genuine 80 per cent flour. To remove by sifting "20 per cent of the husk" in a mill which it is stated "was not working normally" does not furnish the 80 per cent flour advocated in a manifesto published by the League in 1909, and signed by over fifty medical and scientific men.

The flour so advocated is an 80 per cent straight-run flour, including the germ and fine middlings, but should not retain any of the husk, so that it may combine the maximum of nutriment with the minimum of indigestible woody fibre. It is described by Dr. Robert Hutchison as "certainly superior to ordinary white bread from a chemical point of view, whilst it is in no way inferior to the latter in digestibility and capability of absorption." Genuine 80 per cent flour has been largely consumed with beneficial results, but there have been no digestibility experiments made with it. This flour has, however, been used for about ten years with great advantage by the Blue Coat Boys at Christ's Hospital.

There is no proof that the flour used at Cambridge was ground to the necessary fineness. The necessity of this is shown by Digestion Experiments described in U.S.A. *Bull.* 156. It is there shown that Subject 3 digested from coarsely-ground wholemeal only 40.5 per cent of the protein (flesh-forming substance), and that from flour made from the same wheat containing finely ground bran he

assimilated 90 per cent, whilst from 70 per cent flour he only digested 90.6 per cent, a very minute difference when it is borne in mind that whole wheat contains more protein than 70 per cent flour.

In England scientific experiments on the digestion of wholemeal, which Dr. Wynter Blyth continued for a month, were made the subject of a Report to the Royal Society by the late Sir Lauder Brunton, F.R.S., in *Transactions* No. 45. Nothing but finely-ground wholemeal and water was consumed. Rather less protein was assimilated than by the above mentioned Subject No. 3 from flour containing finely-ground bran; but about the same as Subject No. 2 digested. There is, however, no record as to whether the meal used by Dr. Wynter Blyth was ground to the uniform fineness advocated by the League. Other experiments on similar lines are described by Prof. Goodfellow in "The Dietetic Value of Bread." Health was maintained on this exclusive diet, although the absence of milk makes a drastic difference, for the nutrients of a given article are more thoroughly assimilated when it is consumed with some other food. One subject, who was allowed a little olive oil, digested nearly 90 per cent of the total dry substance ingested; whilst another experiment shows that the addition of butter reduced the waste of protein 50 per cent. American experiments mention that more protein was assimilated when milk was used instead of water. There is also reason to believe that green vegetables or other foods containing lime enable the phosphates in cereals to be better utilised. Sir Arthur Church, F.R.S., pointed out long ago that the needful lime to produce the true bone-former, or phosphate of lime, from the phosphates of magnesia and potash in wholemeal, is freely furnished by green vegetables, and if these are taken an interaction may go on in the body by which the essential phosphate of lime is formed. As a practical illustration of this fact it may be mentioned that rabbits fed on oats alone developed thin fragile skeletons, while similar animals fed upon oats and meadow grass, which contains a large amount of lime, produced normal bones.

The American experiments were only made for two and four days upon a very limited number of people, who also consumed considerable quantities of milk. The Cambridge experiments lasted for seven days, whilst those reported to the Royal Society lasted four weeks. But these experiments are too limited in their scope to base on them far-reaching statements about the digestibility of various kinds of bread. Some people may not be able to digest any kind of brown bread, but practical experience shows that the majority can assimilate wheatmeal when it is ground to a uniform fineness. Bread containing 88 per cent of the grain has been used for over forty years in Government institutions. This additional amount would not only increase the available wheat supply, but would also provide a more substantial and nutritious bread. A smaller quantity would be eaten, for experience shows that finely-ground wheatmeal goes further than 70 per cent flour. People are beginning to find that the Government flour is more satisfying than the pre-war bread, and if they eat as much of it they are liable to suffer from indigestion.

With regard to the fibre in wheat, which is only 2½ per cent of the grain, it is well to bear in mind that for many persons, when it is finely-ground, its presence in bread is most beneficial. Food which demands efficient mastication is best for the teeth, stomach, and intestines, and there is reason to believe that the use of over-refined food is having a disastrous effect on the health of the nation.

It is to be regretted that the Report on "The Food Supply of the United Kingdom" only refers to the proteins and calories, and nowhere mentions the phosphates or vitamins, which are equally essential for the maintenance of life. If these two factors had been taken into consideration, the Committee might have seen the advisability of retaining in bread more than 80 per cent of the wheat grain, and especially the germ. This portion, although small, is very important, for it contains useful enzymes to assist

* Report on the Food Supply of the United Kingdom, compiled by a Committee appointed by the Royal Society at the request of the President of the Board of Trade.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, March 29, 1917.

Sir J. J. THOMSON, O.M., President, in the Chair.

PAPERS were read as follows:—

"*The Fourth Colourless Sensation in the Spectrum Sensation Curve when Measured in the Centre of the Retina.*" Sir WILLIAM ABNEY, F.R.S.

At the end of the last century the author carried out a large series of observations on the luminosity of spectra of very low intensity, but only recently he has had an opportunity of working some of them out.

He has some time ago published in the *Phil. Trans.* the three-colour sensations which apparently suffice to account for all the spectrum colours. There was a doubt if in the mixture of the sensations to form these colours some account ought not to be taken of the colour sensation which appears when a coloured ray is diminished in intensity for all colour to be absent and only a colourless residue is left. The author confines himself to the colours received on the centre of the retina, for on the periphery other conditions exist.

The paper shows the method of observation which was employed, and, discussing the results, the author comes to the conclusion that the admixture of the colourless sensation with the three-colour sensations is so small as to be inappreciable, and that the sensation curves given in his paper, to which reference has been made, need no correction on this account.

"*Magnetic Inertia.*" By G. W. WALKER, F.R.S.

It is shown that a magnetised body may be expected to possess magnetic inertia, just as an electrified body possesses electric inertia. In the case of a sphere of radius a and magnetic moment m the inertia for acceleration parallel to the magnetic axis is—

$$\frac{2}{5} m^2 a^{-2} C^{-2},$$

and for acceleration perpendicular to the magnetic axis is—

$$\frac{4}{5} m^2 a^{-2} C^{-2}.$$

(C is the velocity of radiation).

The order of magnitude of this inertia is considered in an astronomical as well as in an atomic connection.

"*The Selective Properties of the Copper-Ferrocyanide Membrane.*" By F. TINKER.

In the present paper the selective properties of copper ferrocyanide have been studied by measuring the change in solution concentration which takes place when the dry colloid is immersed in cane-sugar solutions of various strengths. It is found that the sugar solutions become stronger owing to the fact that the water and not the sugar is taken up selectively by the ferrocyanide. The experimental results lead to the hypothesis that a colloidal hydrate, $Cu_2FeC_6H_3H_2O$, is first formed, and that this colloidal hydrate then takes up still more moisture by adsorption. The amount of "adsorbed" moisture taken up by the colloid decreases as the strength of the solution increases.

The fact that colloidal copper ferrocyanide adsorbs water selectively from cane-sugar solutions without taking up the sugar at the same time supports the author's theory that the property of selective permeability is (in the case of colloidal membranes) a result of preferential adsorption.

It is also shown in the paper that the side of a membrane in contact with pure water has a greater moisture content than the side in contact with sugar solution. This fact supports the hypothesis—first advanced by Graham

digestion. The human system can also probably more readily assimilate the mineral matter of the germ than that of the husk. Experiments on pigeons have shown that when they are fed on wheat deprived of the germ they developed neuritis, but that they remained healthy when it was retained.

But the special advantage of wholemeal, and of 80 per cent flour, to which the Bread and Food Reform League has always directed prominent attention, is the presence of a large quantity of mineral substances, especially phosphates, which form bones and teeth, and nourish the brain, nerves, and tissues.

The Minnesota experiments do not deal with this aspect of the subject, but those made at Cambridge confirm the statements of the League. Prof. T. B. Wood, when describing these experiments in "The Composition and Food Value of Bread," contained in the *R.A.S.E. Journal* in 1911, states.

The 80 per cent bread contained rather more than twice as much phosphoric acid as the white bread. The percentage digested was exactly the same in the two cases, 52 per cent. It follows therefore that the 80 per cent bread supplied to the tissues twice as much phosphoric acid per day as the white bread.

Wholemeal contains four times more phosphoric acid than patent white flour. The Bread and Food Reform League has always taught that when the meal is ground to a uniform fineness a very large proportion of this can be assimilated. Digestion experiments by Prof. Goodfellow showed that in "wholemeal bread containing very fine particles of bran nearly 60 per cent of the ash was dissolved." Opinions vary as to the amount of phosphates required, but as they are of such vital importance, especially for the young, and as Nature does not work in minimums, it is judged safer to have an abundant supply of such essential elements. Dr. Wiley, of America, states in his recent book, "Not by Bread Alone," "There is no longer any doubt of the fact that the demineralisation of our foods, especially the cereal foods, is unscientific, unwise, and unnecessary. A generous mineral diet, as Nature has prepared it, is a necessity for the growing child and a desirability for the grown person."

Finely-ground wholemeal and genuine 80 per cent flour, when made from the same wheat, have more protein than fine white flour, a larger amount of valuable phosphates, and the essential vitamins, which are eliminated from fine white flour. Their adoption will help to improve the general public health, promote temperance, and prevent a great deal of illness.

As bread constitutes the principal diet of many poor children, it is of vital importance that they should be able to obtain it in its most nourishing form, so that they may be better able to maintain health and strength, and thus help to secure a strong vigorous race to carry on the work of a great Empire.

MAY YATES

(Hon. Sec. Bread and Food Reform League).

3, Clement's Inn, London, W.C. 2

Action of Magnesium and Zinc upon Dichloromethylarsine.—Enrique V. Zappi.—Magnesium has no action upon dichloromethylarsine in presence of ether, but if water is added a violent reaction occurs, gases are evolved, and a precipitate appears. Upon analysis the mixture of gases was found to have the following composition:—

CH ₃ AsH ₂		33.3 per cent
H ₂		60.0 "
CH ₄		2.6 "
N ₂		4.0 "

The precipitate is methylarsenic, (CH₃As)_x. Zinc gives the same reaction.—*Anales de la Sociedad Quimica Argentina*, iv., No. 15.

on experimental grounds—that osmosis across a membrane takes place because pure water induces a greater moisture pressure and concentration inside the membrane than the solution does.

"X-Ray Analysis of the Crystal Structure of Rutile and Cassiterite." By C. M. WILLIAMS.

"Discontinuous Fluid Motion." By J. G. LEATHAM, D.Sc.

The subject of the paper is the flow, with free streamlines, of infinitely extended fluid past a finite obstacle with a sharp prow and curved sides. The methods of Levi-Civita, Cisotti, Villat, and Levy are compared with the writer's own method, and translated into formulations by curve factors.

The independent procedure by curve-factors is to establish functional relations between three complex variables, namely, the variable z of the geometrical configuration, the variable w of velocity potential and stream-function, and an intermediate variable ζ such that the relevant regions in the z and w planes correspond to the upper half-plane of ζ . If the points of departure of the free stream-lines correspond to $\zeta = \pm a$, and the prow to $\zeta = c$, it is shown that the most general (z, ζ) relation is—

$$\frac{dz}{d\zeta} = K(\zeta - c) \{ F(\zeta, \xi) \}^{2\pi} \text{Exp} \left\{ -\frac{1}{\pi} \int_{\xi=-a}^{\xi=a} \log F(\xi, \zeta) d\chi \right\}$$

where K is a constant, $2\pi\chi$ the angle at the prow, χ the inclination to the axis of the z real of the tangent at the point of the boundary where $\zeta = \xi$, and—

$$F(\xi, \zeta) = (\zeta - \xi) \left\{ -\xi - i(a^2 - \xi^2)^{\frac{1}{2}} / \right. \\ \left. - \xi\zeta + a^2 - i(a^2 - \xi^2)^{\frac{1}{2}} (\zeta^2 - a^2)^{\frac{1}{2}} \right\}.$$

For a convex obstacle it is shown that the most forward points at which it is physically possible for the free stream-lines to break away are determined by the relations—

$$\int_{\xi=-a}^{\xi=a} \left(\frac{a+\xi}{a-\xi} \right)^{\frac{1}{2}} d\chi + 2\pi\pi \left(\frac{a+c}{a-c} \right)^{\frac{1}{2}} = 0,$$

$$\int_{\xi=-a}^{\xi=a} \left(\frac{a-\xi}{a+\xi} \right)^{\frac{1}{2}} d\chi + 2\pi\pi \left(\frac{a-c}{a+c} \right)^{\frac{1}{2}} = 0,$$

and it the stream-lines break away at these particular points they osculate the obstacle there.

"Theoretical flow" in which there is discontinuity and a wake in irrotational motion is compared with "actual flow" in which there is a wake in rotational motion.

SOCIETY OF CHEMICAL INDUSTRY. (LONDON SECTION).

Ordinary Meeting, April 2, 1917.

Mr. ARTHUR R. LING in the Chair.

AFTER the reading of the Minutes, Mr. W. F. REID said that the Chairman's statement at the last meeting that the Sectional Committee had unanimously decided not to employ a reporter at the meetings did not appear in the minutes.

The CHAIRMAN pointed out that a similar statement had been made by him at the February meeting, and that this had been placed on the minutes which had been passed at the last meeting.

The Minutes were then formally passed.

The following papers were read:—

"Further Notes on the Action of Acetic Acid on Aluminium." By RICHARD SELIGMAN, Ph.D., and P. WILLIAMS.

The present communication is a continuation of the authors' previous work on the subject.

The action of boiling acids of lower concentrations has

been found to conform to that of the more concentrated acids previously examined, and it has been found that the rate of dissolution of the aluminium rises continuously until the concentration of the acid falls to 1 per cent. With the more dilute acids it was found that the rate of dissolution was increased by the presence of the products of the interaction. The influence of this factor grew very rapidly with increasing dilution, so that in the case of 1 per cent acetic acid the rate of dissolution rose as the experiment proceeded to more than five times its initial value. It is not yet possible to assign a definite cause to this phenomenon, but it is obvious that a practical deduction can already be made from the facts observed. Where aluminium vessels are to be used in connection with dilute acids, the greatest care must be taken in their design to avoid small recesses or pockets in which the circulation of the contents cannot take place freely, and in which, therefore, the products of the interaction can accumulate. Attention has been called to this fact in considering the effect of other acids on aluminium (*Journ. Soc. Chem. Ind.*, xxxv., 665), and the correctness of the view now expressed is fully borne out by experience in practice.

In all cases where the action of boiling acetic acid of whatever concentration has been examined, the attack is uniform and no evidence of local action has been observed. The only exception is the peculiar case of anhydrous acetic acid described in the previous communication.

The rate of attack by cold acetic acid is, in general, small. As in the case of boiling acids, the rate of dissolution increases with increasing dilution of the acid. The highest rate so far noted took place with a solution containing 0.02 per cent acetic acid. Local action was also noted in the case of very dilute acid exposed to intensive aeration. In dealing with cold acetic acid it has been possible to show conclusively the effect of oxygen in promoting such local action. Acids which normally cause local action of a serious kind can be made to act perfectly uniformly if the oxygen be entirely removed or if it be replaced by some inert gas.

In the case of cold acids it has also been found that the actual rate of dissolution is raised by the presence of oxygen. Here, again, it may be well to point the practical moral of the observations made. Vessels used to contain solutions of these acids should not be allowed to remain wet for prolonged periods after being emptied and before cleaning. In such cases the metal is exposed to the action of thin films of acid subjected to intense aeration, and, as practical experience has amply demonstrated, local attack frequently ensues. The metal should be purged as soon as possible of any remaining acid, and, where possible, left dry.

One of the original objects of this research was to find an explanation for the fact that in stills used for the distillation of acetic acid the still proper was often found to have a prolonged life, whereas the condensers, notably in their lower part, were frequently subjected to rapid deterioration, due to local perforation. It would appear that the effect of oxygen in promoting such attack affords a sufficient explanation of this phenomenon, because it is precisely at the point where this attack has been observed in condensers that access of oxygen to surfaces bathed in hot acids would take place.

The question arises whether difficulties owing to this cause could not be completely obviated by the introduction of some neutral gas at this point.

The rates of dissolution of aluminium in 10 per cent and 80 per cent acetic acid, both in the cold and at boiling temperature, were compared with the rates obtained after the addition of small quantities of sodium chloride, potassium bromide, potassium iodide, sodium sulphate, and potassium nitrate to the acetic acid.

With 10 per cent acetic acid the addition of up to 1 per cent sodium chloride, potassium bromide, potassium iodide, or potassium nitrate has been found to be practically negligible in the case of boiling acid, whereas an equivalent amount of sodium sulphate raises the rate

of dissolution appreciably. In cold to per cent acid, however, 1 per cent of sodium chloride is sufficient to raise the rate of dissolution tenfold, whereas potassium bromide effects a much smaller increase in the rate of attack, and potassium iodide and nitrate none at all. 0.5 per cent of sulphuric acid, in the form of sodium sulphate, raises the rate of dissolution fourfold in the case of 10 per cent acetic acid at the ordinary temperature.

In the case of 80 per cent acetic acid in the cold, 1 per cent of sodium chloride raises the rate of dissolution from 3.6 to 270 mgrms. of aluminium dissolved per 100 sq. cm. per twenty-four hours. The same amounts of potassium bromide and iodide increase the rate of dissolution approximately tenfold; 0.5 per cent of sulphuric acid, in the form of sodium sulphate, cannot be said to have any effect on the rate of attack by 80 per cent acid in the cold; and potassium nitrate reduces the rate of dissolution to a fourth of its previous value. The most serious effect of the addition of impurities is noted in the case of 80 per cent acid at boiling temperature. Here the rate of dissolution is raised by the addition of 1 per cent of sodium chloride from 290 to 16,000. By 1 per cent of potassium bromide the rate is only increased from 290 to 485, whilst potassium iodide and nitrate may be said to have no effect. 0.5 per cent of sulphuric acid, in the form of sodium sulphate, does somewhat increase the rate of attack.

The form of attack by acids to which the salts named were added appears to be of considerable importance. In general it may be stated that acids which without addition attack aluminium in a uniform manner are not affected by the addition of these salts except that where the rate of attack is raised considerably etching of the surface may be observed. Where, however, the acids alone cause local action, such local action is generally promoted by the presence of halogens, but retarded by the presence of small quantities of sulphuric acid, and absolutely inhibited by as little as 0.1 per cent of nitric acid.

It has also been found that small quantities of nitrates may largely or entirely neutralise the effects of the presence of chlorides.

DISCUSSION.

Dr. C. A. KEANE asked if the authors had noticed anything in the action of acetic acid which might have a disturbing effect. The generation of hydrogen might cause the formation of aldehyde, which would be difficult to detect in the presence of acetic acid. The formation of aldehyde would not occur with the dilute acid. Oxygen acting as a catalyst with aldehyde and acetic acid present might have a very important effect.

Mr. E. J. BOAKE thought that the fact that the action of acetic acids of various strengths was not uniform pointed to an effect of the purity of the aluminium. On one occasion, when a thermometer had been broken in an aluminium still, a hole had eaten right through the metal at the point where the mercury had been in contact, the hole being larger than the drop of mercury, so that corrosion had taken place over a larger area and permeated the metal in the neighbourhood.

Mr. W. C. REYNOLDS asked whether the presence of small traces of ammonia had any effect on the action of various substances on aluminium.

A MEMBER said it would be interesting to know the composition of the aluminium used in the experiments.

Mr. E. T. BREWIS said that he would like to know if the authors had made any experiments on the action on aluminium of a fairly pure water highly aerated.

Dr. A. C. FRYER asked whether the figures given for dilute acetic acid might be safely taken as applicable to butyric, propionic, and the lower fatty acids generally.

Mr. W. C. HANCOCK considered that the specimens shown indicated that oxygen was the cause of the pitting, but he was also in agreement with Mr. Boake that the action was due to some impurity in the metal. Had the authors made any experiments in which the aluminium had been partly exposed to the air and partly immersed in the acid

Mr. BREWIS enquired whether the authors had noticed any difference in the behaviour of aluminium treated in various ways—e.g., cast, hammered, or rolled—and whether this metallurgical treatment causes any variation in the corrosion referred to?

Dr. S. MIALI asked if the authors proposed to investigate the action of acetic acids on other metal. The action on aluminium reminded him of the variations in the action of acetic acid on lead.

Dr. SELIGMAN, in reply, stated that they had never met with any purer aluminium than the samples they had experimented with. The possible action of impurities had not been lost sight of, and he wished that a sample of the absolutely pure metal was obtainable. With regard to the action of mercury, that metal formed an alloy with aluminium, and although amalgamation might occur at one point the area of action was greater and deeper, and a hole might be eaten right through the vessel. Aluminium containing 0.5 per cent of copper was not attacked by mercury at all. In reply to Dr. Keane he said that acetaldehyde was formed, but it was difficult to realise how a product of reduction should form the means of attack unless it was suggested that the re-oxidation of the aldehyde might explain it. He did not think that oxygen was the main cause of pitting, but that it was necessary for pitting. The action of the lower fatty acids in general was still under investigation. He did not propose to undertake the investigation of the action of acetic acid on other metals at the moment.

"Nitrated Castor Oil." By R. BRIGHTMAN.

The author obtained nitrated castor oil by the action of warm dilute nitric acid on castor oil. The nitrated castor oil so obtained is a reddish brown viscid oil, soluble in acetone, ether, alcohol, and acetic acid, but insoluble in carbon disulphide. It has a specific gravity of about 1.05, and is best characterised by determining its nitrogen content by a modification of the Kjeldahl process. The percentage of nitrogen is usually about 3.0. The author concluded that the nitrated oil consists of the triglyceride of the nitric ester of oxidised ricinoleic acids. This view rests mainly on the facts that all the nitrogen is removed on saponification, the drop in the iodine value on nitration, and the proved presence of complex oxidised acids.

DISCUSSION.

Mr. W. C. REYNOLDS asked if the author had observed the formation of lactone compounds during the nitration, and whether the saponification tests were carried out in alcoholic or aqueous solution.

Mr. BRIGHTMAN replied that the only method of determining the composition of the product was to ascertain its molecular weight, but up to the present he had not found a reliable method.

Mr. WALTER F. REID was glad to hear that the subject was being worked upon, because the nitro-compound of castor oil ought to be of use in industry. Nitration carried out with weak acid was incomplete. The acid should have been of sp. gr. 1.5. The presence of water caused oxidation and the formation of free fatty acids. The nitrogen content should be between 1 and 5 per cent; certainly over 4 per cent. The best test he had found for nitrated castor oil was the specific gravity. The author's figure, 1.05, agreed fairly well with those he had found—namely, 1.127.

Physical Society.—The next meeting of the Physical Society will be held at the Imperial College of Science, Exhibition Road, South Kensington, S.W., on Friday, April 27, 1917, at 5 p.m. The following papers will be read:—"A Note on the General Equation for Wave Motion in an Elastic Medium," by Prof. J. A. Fleming, M.A., D.Sc., F.R.S. "The Effect of Stretching on the Thermal Conductivity of Wires," by A. Johnstone, B.Sc. "Cohesion," by Prof. H. Chatley, D.Sc.

CORRESPONDENCE.

THE DEFINITION OF "MATTER."

To the Editor of the Chemical News.

SIR,—In reply to Mr. F. H. Loring's note on "The Principle of Extended Terms" (CHEMICAL NEWS, 1917, cxv., 159) I should like to say that I entirely fail to see how this so-called principle justifies the definition of "quantity of matter" as "equal to or identical with mass." I venture to suggest that if the expression "quantity of matter" does, indeed, mean nothing more than "mass," then it is an entirely unnecessary expression and may well be deleted from scientific terminology. But the users of the word "matter," as Ostwald, who rightly refuses to employ a word so unnecessary and confusing, points out (*vide* "The Fundamental Principles of Chemistry," 7), generally attach a more intensive meaning to the term than would be the case were "quantity of matter" a mere synonym for "mass." Indeed, Mr. Loring himself, later in this note, writes "we do not yet know whether the negative electron has weight and can be classed as matter," and in the same paragraph refers to "inertia" (which he has already equated to "mass") as a "property" of "matter."

I would, indeed, ask Mr. Loring carefully to consider in his mind what the term "matter" really does mean for him, and I think he will find that it stands for a very complex notion—a notion, moreover, which, being not purely experimental in origin but based upon speculation, is foreign to science and belongs to metaphysics. And, in conclusion, I would add, with reference to Mr. Loring's admonition that "more is to be accomplished by thinking in extended terms and in terms of experiment than by introducing the subtlety of logic," that logic is merely a name for sound thinking, without which nothing can be accomplished save confusion of thought.—I am, &c.,

H. STANLEY REDGROVE.

West Ham Municipal Technical Institute,
Stratford, Essex.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clxiv., No. 5, January 29. No. 6, February 5, 1917.

These numbers contain no chemical matter.

No. 7, February 12.

Absorption of the Ultra-violet Radiations by some Chlorine Derivatives of Ethane, Ethylene, and Acetylene.—MM. Massol and Faucon.—Hexachloroethane, although very rich in chlorine, is relatively transparent to the ultra-violet rays. The absorption for radiations of short wave-length diminishes with the dilution for solutions in absolute ethyl alcohol, but no absorption bands appear. Acetylene tetrachloride shows about the same degree of transparency. Pure ethylene tetrachloride, in a layer 1 mm. thick, absorbs all the radiations from $\lambda = 271$. The authors examined acetylene in solution in alcohol and in pure acetone and acetone diluted with alcohol. The absorption was found to be considerable, having regard to the small quantity of acetylene dissolved. All radiations of small wave-length are absorbed. The transparency increases with the dilution, but no absorption bands were observed.

Mixed Anhydrides derived from Benzoylacrylic Acid.—J. Bougault.—When phenylsacrotic acid is dissolved in water with a slight excess of alkaline bicarbonate and iodine is added, an insoluble iodolactone is precipitated. In presence of a large excess of sodium carbonate no lactone is precipitated, but the phenylsacrotic acid is transformed into benzoylacrylic acid. If a large excess of a sodium salt of an organic acid only slightly soluble in water, benzoic acid for example, is added to the mixture in the last reaction a mixed anhydride is formed, for example, in this case, $C_6H_5.CO.CH = CHCO > O$. The two isomeric α -bromocinnamic acids give similar mixed anhydrides with benzoylacrylic acid, and the anhydrides obtained are not identical but isomeric. It seems probable that a lactone is formed as an intermediate product in this reaction.

Nos. 8 and 9, February 19 and 26.

These numbers contain no chemical matter.

MEETINGS FOR THE WEEK.

- MONDAY, 30th.—Royal Society of Arts, 4.30. (Howard Lectures). "The National Shortage of Iron Ore Supplies," by Prof. W. G. Fearnside.
- TUESDAY, May 1st.—Royal Institution, 3. "Tetanus—Its Prevention, Symptoms, and Treatment," by Prof. C. S. Sherrington.
- ROYAL INSTITUTION, 5. (Annual General Meeting).
- WEDNESDAY, 2nd.—Royal Society of Arts, 4.30. "Herb-growing in the British Empire—Its Past, Present and Future," by J. Chapman Shenstone.
- SOCIETY OF PUBLIC ANALYSTS, 8. "Estimation of Phenacetin and Allied Compounds by means of Hypochlorous Acid," by A. D. Powell. "A Rapid Method for the Determination of Nickel and Cobalt in Ores and Alloys," by W. K. Schoeller and A. R. Powell. "Note on Opium Poisoning Cases," by J. Webster.
- THURSDAY, 3rd.—Royal Institution, 3. "Pagan Religion at the Time of the Coming of Christianity—Misleading Preconceptions—The Raw Material—Dea Roma," by Prof. Gilbert Murray.
- ROYAL SOCIETY. (Grobian Lecture). "The Excitation Wave in the Heart" by Dr. Thomas Lewis.
- FRIDAY, 4th.—Royal Institution, 5.30. "Some Guarantees of Liberty," by H. Wickham Steed.
- SATURDAY, 5th.—Royal Institution, 3. "The Electrical Properties of Gases," by Prof. Sir J. J. Thomson, O.M.

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THE CHEMICAL NEWS

VOL. CXV., No. 2997.

GRAIN SIZE MEASUREMENTS IN METALS, AND IMPORTANCE OF SUCH INFORMATION.*

By ZAY JEFFRIES, B.Sc., Met.E.,
Case School of Applied Science, Cleveland, Ohio, U.S.A.

(Continued from p. 194).

Methods for Measuring Grain Size.

THE methods treated have for their object the determination of the number of grains on a certain area of a polished section of a metal. The grains are in reality polyhedrons, and it might seem logical that a cubic unit should be used for reference. The number of grains per square unit on a surface of the sample raised to the $3/2$ power will give the number of grains per cubic unit. Since this definite relation exists it seems simpler to adopt the square unit for reference.

The following methods will be considered and briefly described:—

1. The Planimeter Method.
2. The Heyn Method.
3. The Intercept Method.
4. The Estimation of Grain Size of Unknown by Comparison with Known Samples.
5. The Author's Method.

(NOTE.—Some of the descriptive matter which follows is taken verbatim from a joint article by the author, A. H. Kline, and E. B. Zimmer, *Bull. A.I.M.E.*, December, 1915).

1. *The Planimeter Method.*—This method may be used in either of two ways. The image of the metal specimen



FIG. 1.—Planimeter Method.

may be projected on to a piece of paper and the grain boundaries traced, as shown in Fig. 1.

The total area divided by the number of grains inclosed will give the average area per grain. The second way, which involves less time, is to trace on the paper just the outside lines bounding the area of a group of whole grains. The number of included grains is then indicated by check marks on the paper, as shown in Fig. 2.

Since the counting of the grains can be done at the time of checking, this way is the shorter. The following example is taken from an actual determination:—

The area found by measuring with a planimeter was 5.92 sq. in. The number of grains inclosed was 61. There-

fore, the average area per grain is $\frac{5.92}{61} = 0.09705$ sq. in.

The observation was made at a magnification of 100 diameters. Then $\frac{0.09705}{100 \times 100} = 0.00009705$ sq. in., which

is the actual area per grain. $\frac{1}{0.00009705} = 103,040$

grains per square inch.

2. *Heyn's Method.*—The Heyn method ("Reports of the Technische Hochschule zu Charlottenburg," *The Metallographist*, vi., pp. 54–63) depends for its accuracy on the assumption that the intercepts of a straight line intersecting a number of grains will be proportional to the

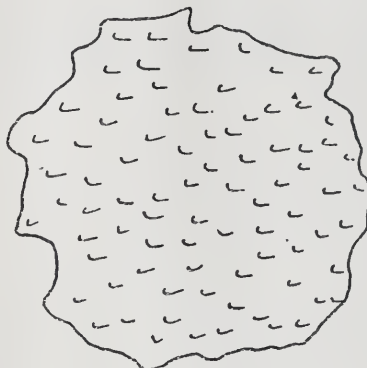


FIG. 2.—Planimeter Method, Modified.

square roots of the areas of the grains. In other words, the square of the average intercept will be the average area per grain. Heyne applies this assumption as shown in Fig. 3.

The number of grains is counted along a line such as AB. The first incomplete grain is counted as one, and the last grain is not counted. By taking a number of lines parallel to AB, and counting the grains intersected by

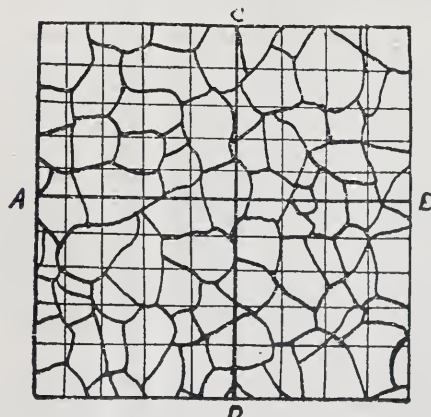


FIG. 3.—Heyn Method.

each, the average intercept in one direction is obtained. The average intercept in the direction CD, at right angles to AB, is obtained in a similar way. The product of the two average intercepts is the average area per grain. For example, suppose the number of intercepts in the direction AB is 79 and the distance 20 in. The average intercept is $\frac{20}{79} = 0.2533$ in. Likewise, suppose the number of

* A Paper read before the Faraday Society, May 9, 1916.

intercepts counted in the direction CD is 72 and the distance is 16 in. The average intercept in this direction is $\frac{16}{72} = 0.222$ in. Then the average area per grain is $0.222 \times 0.2533 = 0.05623$ sq. in. If the magnification is 100 diameters, then $\frac{0.05623}{100 \times 100} = 0.000005623$ sq. in.

actual area per grain, or $\frac{1}{0.000005623} = 177,800$ grains per square inch.

It is not necessary to trace the grain boundaries to apply Heyn's method. A piece of cross-section paper may be used for a screen, and the grains intersecting each line counted and the distance measured.

3. *The Intercept Method.*—The intercept method is based on the same assumption as Heyn's method, but the readings are not confined to series of parallel lines. The method of procedure for determining the grain size by the intercept method is as follows:—In Fig. 4 the line AB is

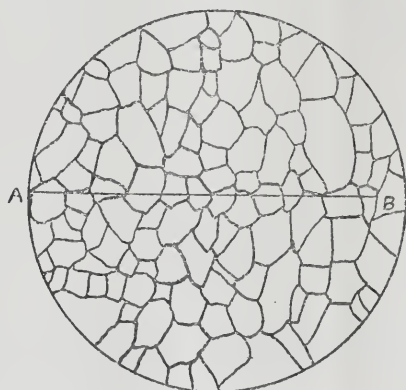


FIG. 4.—Intercept Method.

drawn through the centre of the field. This line intersects 13 grains in a length of 2.58 in. The average intercept per grain is therefore $\frac{2.58}{13} = 0.198$ in. $(0.198)^2 = 0.0392$

sq. in., the average area per grain. If we consider the magnification as 100 diameters, then $\frac{0.0392}{100 \times 100} = 0.00000392$

sq. in., the actual area per grain. The number of grains per square inch is $\frac{1}{0.00000392} = 255,000$. In order to

get the average diameter per grain, sufficient lines should be taken to intersect from 50 to 500 grains.

In actual practice this method is shortened considerably (H. M. Howe, "Life History of Network and Ferrite Grains in Carbon Steel," *Proc. Am. Soc. for Testing Materials*, 1911, xi., 380). An eye-piece with a graduated scale may be used in place of the regular eye-piece. The length of an even number of grains can be measured direct, and the approximate grain size obtained in a short time.

4. *Estimation of Grain Size of Unknown by Comparison with Known Samples.*—This method is used by C. Grard for controlling the work and annealing of copper and brasses ("Industrial Application of Microscopic Metallography for Controlling the Work put on Copper and Brasses," International Association for Testing Materials, Sixth Congress, New York, 1912). He first prepares a set of samples, treated mechanically and thermally under known conditions, and takes micrographs at certain suitable magnifications. The initial set of known samples should include all of the ranges of mechanical working and heat treatment which will be encountered in practice. By taking an unknown sample and comparing its structure

with that of the set of knowns, it is classified according to the size and the shape of the grains. In this way there need be no attempt to determine the number of grains per unit of area, as the relative number of grains may be all the information desired.

The control of carbon and phosphorus in certain iron and steel products will be recognised as a comparative method of grain size determination. These determinations are made macroscopically on the fractures of the samples, and it is surprising how closely the carbon or phosphorus content can be estimated in this manner. The comparison method is the most flexible of all the methods, since it can be used to compare structures of all kinds.

5. *The Author's Method.*—This method has for its object the rapid determination of the equivalent number of whole grains included within a circular portion of an image. It is evident that some of the grains will be completely included within, and some will be intersected by, the circumference of the circle. The former will have no

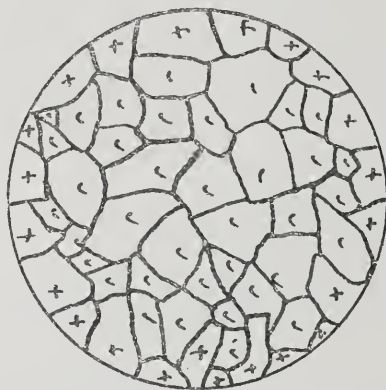


FIG. 5.—Author's Method.

correction factor. The boundary grains, however, will be partly inside and partly outside the circle. In Fig. 5 the grains marked with a check mark are completely included, and those marked x are the boundary grains. The average portion of each boundary grain included within the circle may be found as follows:—The grains completely included within the circle are first counted and checked. Then the boundary grains are checked with a different mark and counted. If the grains are counted as checked, the time of making a determination will be shortened. In Fig. 5 there are 37 included grains and 22 boundary grains. The area of the included grains by planimeter is 1.9 sq. in. The area of the circle (diameter 1.83 in.) is 2.635 sq. in.

$$1.9 : 2.635 = 37 : x.$$

$x = 51.3$, the equivalent number of whole grains within the circle.

$51.3 - 37 = 14.3$, the equivalent number of the whole grains in the inside portions of the 22 boundary grains.

$\frac{14.3}{22} = 0.65$, average portion of each boundary grain within the circle.

If this factor be determined on a large number of samples, it may be used on unknown samples to find the equivalent number of whole grains within a circular area. If we call this factor y , the total number of grains within a circle is $z + yw$, where z is the number of grains completely included and w the number of boundary grains.

The factor y has been determined empirically on 175 samples. The results are given in Table II.

The average value of the factor y for 175 determinations is 0.581. The same factor can be used for all numbers of grains included within the observed area, but it is recom-

mended that all important determinations have at least 50 grains included within the circle. Since 0.581 is nearer to 0.6 than to 0.5, the author has adopted 0.6 as a general factor for all determinations. It should be noted that an error of 1 per cent in the determination of the whole-grain equivalent of the boundary grains makes an error of less than 0.25 per cent in the final result, since more than 75 per cent of the total area of the circle is occupied by the included grains.

The following is an example of how the factor is used:—

Inclosed grains = 66
Boundary grains = 28
Factor = 0.6

$$66 + (0.6 \times 28) = 82.8 \text{ grains within the circle.}$$

From the magnification, the number of grains per unit of area can be readily calculated.

TABLE II.

Grains completely included.	Average value of y.	Number of determinations.
10—20	0.556	11
20—30	0.582	15
30—40	0.542	13
40—50	0.574	10
50—60	0.590	11
60—70	0.600	12
70—80	0.576	11
80—90	0.577	10
90—100	0.596	10
100—120	0.551	11
120—140	0.618	11
140—160	0.546	10
160—180	0.566	10
180—200	0.558	11
200—230	0.606	10
230—290	0.622	9

6. *Comparison of the Various Methods with the Planimeter Method.*—In making the calculations for the comparison of methods the actual number of grains per unit of area was not figured, the number of grains per square inch on the drawing being sufficient for comparison. The percentage of error was figured in the following manner:—Suppose the planimeter method gave 50 grains per square inch, the intercept method 54.2, Heyn's method 55.6. The percentage of error in the intercept method is

$$\frac{4.2}{50} \times 100 = 8.4 \text{ per cent, and in Heyn's method}$$

$$\frac{5.6}{50} \times 100 = 11.2 \text{ per cent. Tables III., IV., and V. show the comparative results obtained by using the different methods.}$$

No attempt was made to test the accuracy of the ocular comparison method. It is apparent that this method would present the largest errors due to the personal equation.

TABLE III.—Heyn's Method.

Number of determinations..	21
Maximum error (per cent) ..	37.5
Minimum error (per cent) ..	0.41
Average error (per cent) ..	13.05

TABLE IV.—Intercept Method.

Number of determinations..	17
Maximum error (per cent) ..	51.5
Minimum error (per cent) ..	3.82
Average error (per cent) ..	21.9

It will be found that the number of grains as determined by the Heyn and intercept methods is usually greater than by the planimeter method. This should be true for the following mathematical reason:—

The square of the mean of any group of miscellaneous numbers is always less than the mean of the squares of those numbers. The following example illustrates this condition:—

Suppose that the lengths of the grain intercepts when cut by a straight line are in the ratio of 1, 2, 3, 4, and 5. The mean of this group of figures is 3 and its square is 9. The mean of the squares of this group of figures is 11. Taking the mean of the squares as the most probable figure for mathematical accuracy, the square of the mean, which is the figure used in the Heyn and the intercept methods, is only 8.8 per cent. By either of these methods, therefore, the indicated area per grain would be low, which would make the number of grains per unit of area high. The greater the difference in magnitude of the individual numbers in any group the greater will be the error due to this cause. For example, if we take simply the first and last figures in the above group, namely, 1 and 5, the mean will be 3 and the square of the mean 9, yet the mean of the squares is 13. Assuming 13 as 100 per cent, the figure 9 would represent only 69.2 per cent of the proper area. From this it would seem that the larger the grain used in either the Heyn or the intercept methods the greater would be the percentage of error, since some grains will be intersected near the edge, thus making the minimum intercept approximately the same for all sizes of grains, while the maximum intercept will increase as the size of the grain increases.

The results obtained indicate that no correction factor can be applied to either the Heyn or the intercept method with the expectation of compensating for the errors encountered. The safest way would be to measure each intercept, square it, and take the mean of the squares. The method cannot be carried out practically in this manner, since the time for making a determination would be excessive.

In the author's method it is suggested that the reason the factor y is greater than 0.5 is that the 0.5 point would be realised more nearly if cords were drawn at the intersection of the circumference of the circle with the grain boundaries. It is apparent that the arc will include a greater portion of a grain than the cord. If this line of reasoning is correct as the size of the circle increases, other conditions remaining the same, the factor y should approach 0.5.

TABLE V.—Author's Method.

Included grains.	Boundary grains.	Factor.	Area of circle.	Author's method. Grains per sq. in.	Planimeter method. Grains per sq. in.	Error per cent.
118	49	0.6	7.068	147.4	146.30	0.8
95	35	0.6	7.068	116.0	123.80	6.3
34	27	0.6	7.068	50.2	49.85	0.7
59	30	0.6	7.068	77.0	76.22	1.0
74	37	0.6	7.068	96.2	94.93	1.3
56	35	0.6	7.068	77.0	73.69	4.5
110	41	0.6	7.068	134.6	137.80	2.3
93	40	0.6	7.068	117.0	116.97	0.0
75	37	0.6	7.068	97.2	94.20	3.2
103	43	0.6	7.068	128.8	134.00	3.9

Average percentage of error, 2.4 per cent.

The average of plus and minus errors in 187 determinations was plus 0.25 per cent. The largest error found was 6.4 per cent, and the average error 2.1 per cent. An average of 30 representative determinations showed that 78.5 per cent of the total area of the circle was occupied by the included grains. This portion is determined accurately by the author's method. The factor is used in determining only 21.5 per cent of the number of grains, so that an error of 5 per cent in estimating the boundary grain portion makes an error of slightly over 1 per cent in the final result.

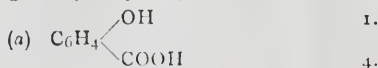
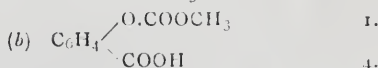
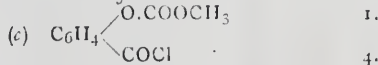
To be continued).

FISCHER'S SYNTHESIS OF DEPSIDES AND TANNING SUBSTANCES.*

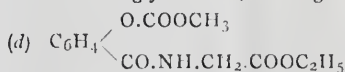
By Prof. J. A. WILKINSON, M.A., F.C.S.

THE work carried out by Prof. Emil Fischer and his pupils on the polypeptides, which has contributed so largely to the extension of our knowledge of the proteins and their derivatives, is well known, and led indirectly to the work outlined here, culminating in the synthesis of a substance which possesses practically all the properties of tannic acid, and the preparation of a large number of others strictly allied both in properties and composition. Whilst engaged in the synthesis of polypeptides of tyrosin, he desired to prepare a chloride of chloracetyl tyrosin in order to obtain glycyl tyrosyl glycine. On treating with phosphorus trichloride it was found that the free phenol groups present in the molecule caused trouble, and hence he conceived the idea of fixing them in the meanwhile by means of a group, which could afterwards be removed easily and the original phenol group restored. For this purpose the methyl ester of chlorcarbonic acid, Cl.CO.OCH_3 , was used, the hydrogen of the phenolic hydroxyl being replaced by the methyl carbonato group $-\text{CO.OCH}_3$. The methyl carbonato compounds thus produced were then treated with phosphorus chloride, yielding the methyl carbonato-chlorides, which on subsequent treatment with sodium hydroxide re-introduced the original phenol group. The success of this procedure in the case mentioned led to its trial with the phenol carboxylic acids, the results of which are detailed in a series of brilliant papers entitled "The Methyl Carbonato-derivatives of Phenol Carboxylic Acids, and their Use for Synthetic Operations," the first of which appeared in 1908. In these it was shown that the chlorides of these acids were unobtainable by the ordinary methods of preparing acid chlorides, owing to the fact that the phosphorus chlorides attack both the hydroxyl and carboxyl groups, and yield products of variable composition, as had been shown previously by R. Anschütz. The reactions which take place may be exemplified thus:—

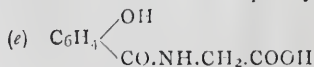
Starting with parahydroxybenzoic acid—

By the action of Cl.CO.OCH_3 —By the action of PCl_5 —

Which combines with glycine ester, forming—

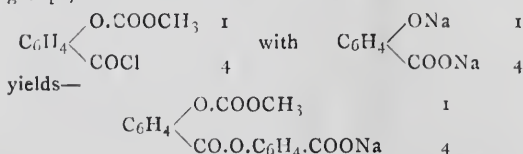


which, with dilute alkali and subsequently acid, yields—

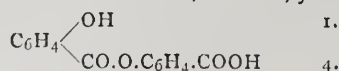


Parahydroxyhippuric acid

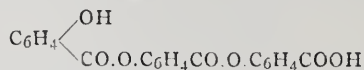
Similarly, in the case of the phenolcarboxylic acids themselves, union takes place between the OH and COOH groups, thus—



which, with alkali and then acid, as above, yields—



This is the simplest type of a new series of substances which have been named by Fischer the "Depsides," from the Greek word $\delta\epsilon\psi\iota\delta\epsilon\iota\varsigma$, to tan, since many of these substances possess properties similar to the tanning materials in common use. From this substance and *p*-hydroxybenzoic acid is obtained in a similar manner—



and so on. According to the number of phenolcarboxylic acids coupled together, we distinguish between di-, tri-, tetra-depsides, just as in the case of the polysaccharides and polypeptides. Up to 1913, Prof. Fischer had prepared in a state of purity twenty-eight di-depsides, two tri- and two tetra-depsides.

These substances are by no means new, a few of the simpler ones having been prepared formerly. H. Schiff and others prepared from gallic acid, by means of silver nitrate or arsenic acid, and then phosphorus oxychloride, a substance to which the name digallic acid was given and formula $\text{C}_{14}\text{H}_{10}\text{O}_9$, supposed to be identical with tannic acid, a statement found in text-books even to-day, but which, in the light of Fischer's work, cannot be maintained. This investigation was extended later to a whole series of other phenolcarboxylic acids, but unfortunately most of the substances he obtained were amorphous, and hence have been criticised, especially with respect to uniformity of composition. It is worthy of note, however, that these researches gave rise to the commercial preparation of artificial tanning materials. Further, Klepl, in 1883, by heating parahydroxybenzoic acid, obtained both the above substances, but this simple method is inapplicable in other cases.

In addition to the depsides, which are pronounced acids, the phenol carboxylic acids can also form neutral anhydrides.

The introduction of the methyl carbonato group, by use of the methyl ester of chlorcarbonic acid, is not difficult to effect in the case of the meta- and parahydroxybenzoic acids, and this is found to be general if the phenol groups are in these positions with respect to the carboxyl group. At the same time the number of hydroxyl groups present makes but little difference. The hydroxyl groups in protocatechuic and gallic acids are completely converted with slightly more than the theoretical quantity of methyl chlorcarbonate. But the case is quite different if the hydroxyl-group stands in the ortho-position to the carboxyl-group. The replacement sometimes succeeds if excess of the chlorcarbonic ester be used in aqueous alkaline solution—e.g., with orsellinic and pyrogallol carboxylic acids—but examples of this are rare. The general method used in this case was first employed by F. Hofmann for the preparation of orthoethylcarbonatobenzoic acid by the action of ethyl chlorcarbonate on a mixture of salicylic acid and dimethylaniline in an indifferent solvent—e.g., benzene. Prof. Fischer used this method to convert the two hydroxyl groups in gentisic and β -resorcylic acids into methyl carbonato groups, from which the chlorides were afterwards prepared (*Ber.*, 1909, 215). More difficulty was experienced with the phloroglucin carboxylic acids, but this was overcome by using large excess of methyl chlorcarbonate and dimethylaniline, and afterwards treating with bicarbonate in acetone solution.

If the carboxyl group is not united directly to the benzene ring, e.g., orthocoumaric acid, no difficulty is experienced, and the reaction proceeds well in aqueous alkaline solution.

By these methods a large number of the phenol carboxylic acids have been completely converted into the corresponding methyl carbonato compounds. Partial replace-

* From the South African Journal of Science, xiii., No. 4.

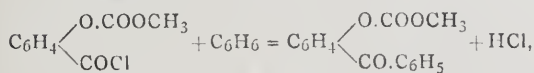
ment may also occur, this being chiefly dependent on the active mass of the reagents used, but in these cases also it has been found that the para-compound is the one most generally formed, and next the meta-derivative.

The complete re-conversion of the methyl carbonato group to the phenol group is easily carried out by using excess of cold aqueous alkali, and more slowly with normal ammonia solution; but in the latter case the group splits off, not as carbonate, but as urethane, $\text{NH}_2\text{COOCH}_3$. Neutral alkali carbonate acts even more slowly, whilst bicarbonate is apparently indifferent, and hence is useful for dissolving out the acids. Partial removal also takes place with smaller quantities of alkali, the para-groups being first attacked. By this means the monomethyl carbonato compounds can be prepared from the dimethyl carbonato compounds.

The chlorides of these methylcarbonatocarboxylic acids are prepared by the action of PCl_5 either by gentle heat or shaking the acid with PCl_5 and dry chloroform. Generally speaking, they crystallise well, and show the reactions of acid chlorides, such as benzoyl chloride. By replacement of the methylcarbonato group with the original phenol group, the acid chlorides themselves are obtained. The latter have been obtained directly by H. Meyer; but the products he obtained do not crystallise, remaining as oils, and cannot be compared in importance with those obtained as above by Fischer's method. Further, the chlorides of the completely methylated or acylated phenolcarboxylic acids have been known for a long time, and are stable enough to serve for synthetic purposes, but the removal of the methyl or acyl groups afterwards is difficult.

These methylcarbonato acid chlorides have been used for the following syntheses:—

1. With alcohol they form esters, which on subsequent saponification with alkali are changed to the esters of the free phenolcarboxylic acids. This reaction is of especial importance in the case of the polybasic alcohols of the sugar class, as will be exemplified later.
2. With the amino-acid esters in aqueous alkaline solution, they couple themselves directly, as shown in the case of parahydroxyhippuric acid given above. By this means the isomeric orthosalicylic acid has also been prepared.
3. In the presence of aluminium chloride direct union with benzene takes place, as shown in the syntheses of paraoxybenzophenone; thus—



saponification removing the methylcarbonato group. It is noteworthy here that pyrogallol carboxylic acid yields 2.3.4-trihydroxybenzophenone, identical with alizarin yellow A, whose formula, $\text{CO}[\text{C}_6\text{H}_2(\text{OH})_3]_2$, is now conclusively established.

4. The free phenolcarboxylic acids also react directly with the chloride, forming di-depsides, as already shown, and similarly for tri- and tetra-depsides.

In the case of the di- and trihydroxybenzoic acids containing two and three hydroxy groups, isomeric methylcarbonato depsides result, as also complicated derivatives, which are difficult to separate and purify. So far one case only has been fully worked out—the coupling of dimethylcarbonato orsellinic acid chloride with orsellinic acid necessary for the synthesis of lecanoric acid.

Di-gallic, di-protocatechuic acids, as well as a large number of other di-depsides, have been prepared by this method, and their constitution thus clearly established. Many of these substances, as has already been mentioned, show the reactions of the tannins in greater or lesser degree.

On the subject of these chlorides, Prof. Fischer further remarks that their applicability for synthetic purposes is

by no means exhausted, and that they will yet prove of great service in cases where benzoyl chloride has hitherto been found of service, and where the phenol groups may be easily restored by gentle saponification. He further recommends the use of the chloride of methyl carbonato ferulic acid as suitable for the synthesis of curcumin, which has not yet been worked out.

The re-conversion of the methylcarbonato group to phenolic hydroxyl is possible by using cold dilute alkali or aqueous ammonia at 20°C ., the reaction being generally completed in half to three quarters of an hour with normal or semi-normal solutions. If alkali be used, sufficient is added to neutralise the carboxyl group, and then 2 molecules NaOH for each methylcarbonato group. If the weaker ammonia be employed, a large excess is required.

The di-depsides hitherto investigated are crystalline substances difficultly soluble in cold water, but soluble in bicarbonate solution, acid in reaction, and melt with decomposition. Like the simple phenolcarboxylic acids, they give colorations with ferric chloride. They react with diazo methane, forming completely methylated compounds, which crystallise extremely well and melt at a lower temperature than the depsides without decomposition. Owing to these properties they have been useful for the purposes of identification.

The first paper directly concerned with tannin appeared in the *Berichte* in 1912, and was entitled "Tannin, and the Synthesis of similar Substances." It begins with an historical introduction discussing briefly the various researches published up to that time. These had not resulted in the establishment of a definite composition or formula for tannin which would defy criticism or investigation, but certain facts had been ascertained which Prof. Fischer thought it necessary to confirm or reject as a result of his own investigations.

(To be continued).

CITIZENSHIP AND HEALTH QUESTIONS IN WAR TIME.*

By CHARLES PORTER, M.D., B.Sc., M.R.C.P.Ed.

THE lecturer said that while, as was always the case in war time, there had been an awakening to the importance of the relationship between citizenship and public health, there was still a necessity for great efforts to be made for maintaining the interest of the citizen in health questions if the best results were to be obtained. In the Boer War the awakening that took place led to the establishment of the School Medical Service and the giving of attention to the health of the school child. So far, this war had directed attention to the necessity for taking action on behalf of motherhood and young childhood, and with a view to the prevention of measles, which took so large a toll of the young. Efforts also were being made to bring the venereal diseases under control and to stamp out what was a most serious threat to the manhood of the nation.

Apart from these, possibly the clearest sign of awakened citizenship was the widely felt desire for the establishment of a separate Ministry of Health. Of recent years the field of public health work had widened tremendously, and yearly was widening to such an extent that centralisation of all the activities was essential. At the present moment effort was too diffused and there were very distinct signs of waste, not only in respect of efficiency, but also of time and money. Even if reorganisation and co-ordination came about, however, the best results would not be obtained, unless the citizen recognised that his interest in public health must be continuous. Spasmodic awakenings were all very well, but something more was required.

He believed that it was necessary to teach the citizen

* Abstract of a Lecture delivered at the Royal Institute of Public Health, April 25, 1917.

something of citizenship, and to show him how much public health did for him and how much he could do for it. Much of the teaching could be done by those engaged in the public health service, and he suggested that the time had come for a recognition by health workers of the fact that largely they were propagandists and that the propaganda work was waiting to be done.

REPORT OF THE ROYAL ONTARIO NICKEL COMMISSION.

THE Royal Ontario Nickel Commission, appointed by the Ontario Government on September 9, 1915, "To Investigate the Resources, Industries, and Capacities in connection with Nickel and its Ores," has presented its Report.

The Commissioners are:—Geo. T. Holloway, Associate of the Royal College of Science, London, and Vice-President of the Institution of Mining and Metallurgy, an English metallurgical expert of high repute; Dr. W. G. Miller, Provincial Geologist; and McGregor Young, K.C., a well-known barrister of Toronto; Thomas W. Gibson, Deputy Minister of Mines, acted as Secretary.

A little pink slip at the front of the Report informs the reader that in order that the Report might be placed before the Legislature at the earliest possible date, 150 advance copies have been struck off without the last chapter (which is a Bibliography of Nickel) and the Index, but both of these will be included before the Report is issued to the public at large. The Report proper is a bulky volume, containing over 600 pages, and is well illustrated with cuts, diagrams, and maps. In addition there is an appendix, of 219 pages, which contains the evidence of the witnesses who testified before the Commission, and a number of papers, memoranda, and other matter pertinent to the inquiry.

The Commissioners print a summary of the Report, and their conclusions on the main points of the investigation at the forefront of the volume, and thus enable the reader to obtain the gist of the Report without difficulty. After references to the various countries they visited, including the United States, Great Britain, France, Norway, Cuba, Australia, and New Caledonia, and to numerous mines, works, plants, smelters, &c., on this side of the Atlantic and on the other, and also to their interviews and conversations with Mr. Bonar Law, then Secretary of State for the Colonies, and other British Government officials, the Commissioners go on to say:—

"The two questions that have been uppermost in the numerous discussions that have taken place concerning Ontario's nickel industry during the last twenty-five years, are:—(1) Can nickel be economically refined in Ontario? and (2) Are the nickel deposits of Ontario of such a character that this province can compete successfully as a nickel producer with any other country? It will be seen that the Commissioners have no hesitation in answering both of these questions in the affirmative."

The Report goes on to state that the Commissioners are of the opinion:—

1. "The nickel ore deposits of Ontario are much more extensive and offer better facilities for the production of nickel as a low cost than do those of any other country. Nickel-bearing ores occur in many parts of the world, but the great extent of the deposits in this province, their richness and uniformity in metal contents, and the success of the industry, point strongly to the conclusion that Ontario nickel has little to fear from competition.

2. "Any of the processes now in use for refining nickel could be successfully worked in Ontario, and conditions and facilities are at least as good in this province as in any other part of Canada.

3. "In view of the fact that practically no chemicals

are required, that there is a much more complete saving of the precious metals, especially platinum and palladium, and that electric power is cheap and abundant, the most satisfactory method of refining in Ontario will be the electrolytic.

4. "The refining of nickel in Ontario will not only benefit the nickel industry, but will promote the welfare of existing branches of the chemical and metallurgical industries, and lead to the introduction of others.

5. "The methods employed at the Ontario plants of the two operating nickel companies are modern and efficient, although there are differences in both mining and smelting practice. It is the consistent policy of both companies to adopt all modern improvements in plant or treatment. Even during the present time of acute pressure, the Canadian Copper Company has materially increased its output without substantial enlargement of its plant, and the losses in smelting are less, both at Copper Cliff and the Mond plant at Coniston, than they were a year ago. These companies have each had their experimental stage, neither has asked nor received any Government assistance, and both have earned the success which they have achieved.

6. "The present system of mining taxation in Ontario is just and equitable and in the public interest, and is the best system for this province. Any question of change is rather one of rate than of principle. This important question is dealt with at some length in Chapter XII.

7. "Experiments have been undertaken by the Commission in the production of nickel-copper steel direct from Sudbury ore, and also in the electrolytic refining of nickel. Certain improvements in the latter process have been made the subject of application on behalf of the Government of Ontario for patents in Canada, United States, and Great Britain."

Public interest in the nickel question has been, and continues to be, very keen. It has been a matter of popular belief that Ontario has a practical monopoly of the world's nickel, and there has been something like exasperation in the public mind because of the fact that none of the nickel mined in Ontario was refined in Canada, but that it was being sent abroad, and mostly to the United States, for final treatment.

The opening chapter of the Report deals with the agitation which has gone on from the beginning of the industry in favour of the refining of nickel in Ontario, the various steps which governments or parliaments have from time to time taken to realise this desire; the negotiations with the Imperial Government for the same purpose are also summarised. The offer of the Ontario Government to the British authorities in 1891 to give the latter a substantial if not a controlling interest in the nickel mines of the province, if they would agree to establish refining plants and make nickel-steel here, is recalled. Doubt is cast, not upon the good faith of the offer, but upon the possibility of implementing it, if it included only the nickel deposits at that time remaining in the possession of the Crown. It is stated that most of the great deposits now being worked had already been parted with before the date of the offer. Nevertheless, the Report says that the action of the Government was a notable one, arguing remarkable insight into the future, and "had the offer been met with an equal degree of imagination on the part of Great Britain it is not easy to say what the results would have been. Even with the deposits found since 1891 a good deal of nickel could have been obtained, and it could always have been possible to purchase privately-owned properties."

The Commissioners say that at the beginning of their enquiry it was asserted by the companies interested that nickel could not be economically refined in Ontario. They therefore naturally express gratification at the assured prospect of the erection in Ontario of two large plants for the refining of nickel. One is now being constructed by the International Nickel Company of Canada, Limited, at Port Colborne. The company has obtained a site of 400

acres on which 2000 men are now at work, and is erecting a plant whose initial output will be on the basis of 15,000,000 lbs. of nickel per annum, provision being made for doubling or quadrupling this capacity. The matte to be refined here will come from the smelters of the Canadian Copper Company at Copper Cliff, for the treatment of which there will be required bituminous coal, coke, fuel-oil, nitre-cake, and other chemicals and materials, estimated at 100,000 tons annually. The plant is expected to be in operation and turning out refined nickel in the autumn of the present year.

The second refinery is that of the British America Nickel Corporation, Limited, a company controlled and largely financed by the British Government, which has purchased the large Murray mine, the Whistle, and other deposits in the Sudbury region. This refinery will probably be erected at the Murray mine, which is about three miles from Sudbury. The refining process employed will be the electrolytic, otherwise known as the Hybinette process, from the name of the inventor who uses it in the Norwegian works. This plant will have a capacity at the beginning of 5000 tons of nickel per annum.

As to compulsory measures for ensuring that the whole of the nickel output of Ontario should be refined within her borders, the Commissioners say they are advised that the Provincial Legislature has not power to prohibit export or to impose an export tax directly, and that the power of the province in effect to regulate export by differential taxation in favour of nickel refined within the province, is a matter of grave doubt. The completion and operation of these plants, in the view of the Commissioners, especially because of the probable extension of the facilities now being provided, will go far towards a solution of the question of home refining, which has so long exercised the public mind. The output of these refineries, added to the nickel now being produced in England from Ontario matte, will fully meet, if not surpass, the entire requirements of the British Empire.

A custom smelter for nickel ore has sometimes been suggested by individual owners of nickel deposits or small companies. The Report states that the British America Company are prepared to consider this question, and that if such an arrangement could be effected it would answer all probable requirements.

The suggestion has been made in certain quarters that Government ownership would solve many of the questions which have been raised in connection with the nickel deposits. The Commissioners point out that to expropriate the deposits and plants of the Sudbury nickel area would probably cost not less than 100,000,000 dol., a sum approximately equal to the total paid-up capital of all the chartered banks in Canada. They add:—

“There is no certainty that large profits can be made every year from the nickel industry. The present activity is in part due to well understood causes, which it is to be hoped will never recur. In the past the output has had to be curtailed at times. If the price of nickel should fall, profits will naturally decrease. The nickel industry is to a considerable extent dependent for its success on the highly trained and specialised technical men who superintend it, who command salaries far beyond those which are paid in the Government service to the most highly placed employees. Besides, nickel is not a necessity of life, nor an article of universal consumption or use, and the nickel business is in no way comparable to those connected with the operation of public utilities where Government ownership may be beneficial or expedient. In short, there does not seem to be any good reason why the people of Ontario should be asked to adventure so large a sum of money as would be required for the purchase of the nickel deposits and plants.”

The uses of nickel are dealt with in several chapters under the headings—“Properties and Uses of Nickel and its Compounds,” “Non-ferrous Alloys,” “Nickel-steel and

other Alloys of Nickel containing Iron.” The great use of nickel is in the manufacture of nickel-steel, the ordinary form of which contains about 3½ per cent of the metal. As compared with ordinary carbon steel, nickel-steel has much greater strength and ductility, and is used in various forms in a wide range of industrial operations, also in the manufacture of armour-plate, ordnance, projectiles, protective deck plate, gun-shields, and many other articles of nava and military equipment. Large bridges at New York, and over the Mississippi and Missouri rivers, dams, docks, and spillways of the Panama Canal, and other large structures illustrate the usefulness of nickel-steel. For locomotive forgings, marine engines and shafting, wire cables, automobile parts, &c., there is a large and growing use. Many useful alloys of copper and nickel are produced and used for a variety of purposes, such as bullet-casings, for coinage, plumbers' supplies, &c. The use of nickel in the electro-plating of metallic objects is widely known and needs no explanation. As finely-divided metal, nickel is used as a carrier of hydrogen in the manufacture of fats from oils, and this property is largely made use of by soap-makers. Pure nickel is used in coins, in making watch and cigarette cases, and cooking utensils. It is also drawn into wire used in spark plugs and electrical leading-in wires. Purchasers and leading consumers in Britain and the United States express the opinion that the uses of nickel will be extended, and that when normal peace conditions are fully restored the demand will be greater than it was before the war. A reduction of the price would undoubtedly enlarge consumption and require increased production.

Chapter IV., on the Nickel Deposits of the World, contains 191 pages, and is in itself a complete treatise on this subject. The Sudbury deposits are first taken up, and their geology, mineralogy, and composition fully discussed. The extent of the ore reserves is given at 70,000,000 tons of proven ore, and of proven, probable, and possible ore at 150,000,000 tons. Mining methods are described and illustrated. New Caledonia is generally held up as the chief competitor of Ontario in the production of nickel, and the deposits there are dealt with. The ore is different from that of Sudbury and does not contain copper. It is shown that while there is a good deal of nickel in New Caledonia, the mines are small compared with those of Sudbury. The largest mine yet worked contained 600,000 tons; few exceed 250,000 tons, while in Sudbury the large deposits have tonnages ranging up to 45,000,000 tons. The ores as shipped are richer in nickel than those of Sudbury, but are gradually lowering in tenor; they are more expensive to work, are farther away from the markets, and the production is increasing very slowly. While the output of the Sudbury mines has grown ninefold during the last fifteen years, that of New Caledonia has increased by only 20 per cent. The conclusion as to New Caledonia is summed up in the following words:—

“The essence of the whole matter in so far as competition from New Caledonia in the open market is concerned, is the cost of the refined nickel produced from these ores. More than a dozen years ago the cost was approximately 19 cents a pound, immediately prior to the war it had not been lowered; at present with excessive freight rates and increased prices for supplies the cost is much increased. As long as the price of nickel remains about the same as it has been during recent years, New Caledonia will have an important industry. It will probably expand to some extent owing especially to the activities of the newer of the two companies that are shipping ore and smelting on the island; but there is no good reason for believing that the competition from New Caledonia will become any stronger than it has in the past. Should the price of nickel fall to 25 cents a pound or less, New Caledonia will have difficulty in keeping her mines in operation.”

The nickel mines of Norway are dealt with. They are of the same character as those of Sudbury, but poorer in

both nickel and copper. The deposits are small, and the output is not capable of very large expansion. The electrolytic process of refining is employed in Norway, and all the Norwegian nickel since the beginning of the war has been going to Germany.

There are many other countries in the world which contain deposits of nickel ore, including Germany and Austria, France, China, Russia, Egypt, Italy, Tasmania, United States, &c. Most of these deposits appear to be of limited extent. In Madagascar the ores are similar to those of New Caledonia, but have never been worked. In the island of Seboekoe, near Borneo, and in Cuba, there are large and doubtless important deposits of nickeliferous iron ore. In Seboekoe they have never been worked, while Cuba operations have been going on for some seven or eight years. Neither, however, can be regarded as a source of metallic nickel, and the shipments from Cuba do not appear to be increasing.

The Commissioners conclude that while it is true Ontario has no monopoly of nickel, it possesses many advantages over all competitors, or under the present conditions of the market as to prices and trade connections. In any keen competition as to price it is doubtful whether any locality at present known or suggested could compete with Ontario. It is a matter of record that at one time of low prices the leading New Caledonia company was compelled to suspend its dividends. It may be doubtful, further, whether anything but an arrangement of the market between the great interests can prevent the complete domination of the world's trade by the nickel industry of Ontario making the best use of its exceptional resources.

A chapter of the Report is devoted to the history and development of the principal operating companies connected with the industry in Ontario from its inception. The organisation of the Canadian Copper Company is traced, and the merger of 1902 by which the International Nickel Company absorbed that company and the Orford works, and thus united under one control the mines and the refining process, is set forth. A table shows the exports of metallic nickel by the International Nickel Company for the ten years previous to the war, and also for the period from the beginning of the war to December 31, 1916. The former table shows that Germany and Great Britain received the bulk of the exports in pre-war times, and that Great Britain, France, Russia, and Italy have taken nearly all of the overseas shipments since that time, none going to Germany. Prior to the war nickel, in whatever country produced, was sold like any other metal wherever there was a market for it, and was treated solely as an article of commerce without regard to international relations. A schedule is given showing the countries in which the shares of the International Company are held. This covers 89,125 shares of preferred stock and 1,673,384 shares of common stock. The great bulk of the shares are held in the United States, Canada and Great Britain coming next. Only 250 shares of preferred and 452 shares of common stock are held in Germany and Austria. Full details are given of the reorganisation of the International Nickel Company in 1912. On December 31, 1916, the common stock stood at 41,834,600 dols. and the preferred at 8,912,600 dols., making a total share liability of 50,747,200 dols. Another table shows common stock dividends paid from 1910 to 1916 a total of 30,942,238 dols. The profits from 1903 to 1916 aggregated 39,850,356 dols., total assets 61,230,813 dols. Little further allusion is made to the question of any possible exports of nickel to Germany during the war, the Commissioners stating that this question was not within their jurisdiction.

The Mond Nickel Company operates on a smaller scale than if the copper is not too high. Indeed, there is reason to believe that the presence of a limited proportion of copper in steel is beneficial, and also that it is capable of replacing a proportion of the nickel in nickel-steel up to at least one-third of the combined quantity of nickel and copper. Experiments made for the Commission by Prof. Guess, of Toronto University, fully confirmed these con-

clusions. Copper also appears to assist steel in resisting corrosion.

The production of nickel as a by-product was investigated by the Commission. Such production is of considerable importance. By-product nickel comes mainly from the electrolytic refining of blister copper, copper ores almost invariably carrying a small proportion of nickel. About 815 tons of nickel were obtained in 1915 from the refining of copper in the United States, and the tremendous production of copper going on in that country will largely increase this quantity. In addition, scrap metal containing nickel is continually being re-treated and the nickel recovered. The production of by-product nickel, though small in comparison with the output of ores worked for that metal, has much bearing upon possible supplies of non-Canadian nickel for export to enemy or other countries.

The Commissioners point out that the importance of the precious metal contents of the Sudbury ores has not in the past been fully recognised. These consist of gold, silver, platinum, palladium, iridium, and other rare elements. The proportions of those metals which the ores carry are minute, and appear to vary in the several deposits. Roasted matte from one of the companies showed 0.1235 oz. platinum, and 0.197 oz. palladium, 0.0027 gold, and 1.34 oz. silver, while the other company's matte showed platinum, 0.988 oz.; palladium, 0.934 oz.; gold, 0.256 oz.; and silver, 6.155 oz. per ton. Platinum is at present very scarce and the price unusually high; palladium is being substituted for it wherever suited. Both these metals are now worth at least five times as much per ounce as gold. The Orford refining process recovers a much smaller quantity of the precious metals than the Mond and electrolytic processes. The recovery of the metals of the platinum group constitutes an interesting chapter of the Report. It states that the platinum and palladium contained in the Copper Cliff mattes for the year 1916 would be worth 791,600 dols.

Losses in mining, smelting, and refining are discussed in the Report. These are stated to be considerable. Certain losses are inevitable at each of the successive stages of treating the ore. In mining, heap roasting, smelting, converting, and refining such losses cannot be wholly eliminated. In smelting there is not much reason to anticipate that further saving of the metals can be made. The abolition of heap-roasting would make a small saving in nickel and copper. The whole of the sulphur in the ore must be got rid of, and at present all goes to waste. The question of the possible recovery and utilisation of sulphur fumes is given a chapter in the Report. Fumes from the roast heaps are objectionable and injurious, and there is no means of collecting the sulphur given off from the heaps. A million tons of ore contains sulphur enough to make a million tons of sulphuric acid, but sulphuric acid could only be produced at a heavy loss, since the freight charges to markets on so bulky an article would cost more than it is worth.

A chapter is devoted to statistics of nickel production, showing the output of Ontario, New Caledonia, Norway, and other countries.

The important subject of taxation is dealt with in the concluding chapter. The Commissioners were instructed to report upon a just and equitable system for taxing, not only nickel and copper mines, but mines of all kinds. Their report is that the present method of taxation on net profits is the fairest and best. In their opinion the present rate of 3 per cent should not be raised beyond 5 per cent. Gold mining companies occupy a unique position; their product has a fixed price of 20.67 dols. an ounce, and while all other metals have advanced, some of them very materially, the gold companies get no more for their product than before, yet their costs are largely increased by the higher prices for labour and cost of supplies.

The Report seems to cover every conceivable phase of the nickel question, at any rate in relation to industry and trade, and will form a veritable encyclopædia of information for many years to come.

TAKING OUT OF SCIENTIFIC PATENTS.

I AM commanded by My Lords Commissioners of the Admiralty to acquaint you that they have had under consideration the question of what rules, if any, it may be desirable to lay down as regards the taking out of patents, and the payment of remuneration for inventions resulting from the labours of scientists and others who during the war are carrying out special research work on behalf of H.M. Government, whether independently or in co-operation with military, naval, or civilian officers.

2. There are many cases in which the Admiralty supplies valuable information and assistance, and sometimes defrays expenses connected with such researches. On the other hand, the individuals or scientific bodies referred to are in many cases giving their services free of payment and producing most important results.

3. Thus both the State and the individual or scientific body concerned may have legitimate claims to participate in any patent rights which may be obtainable in the product of these labours and in any commercial profit which may arise therefrom.

4. In any case where the result arrived at is of military value, it is obviously necessary that H.M. Government should have the right to keep it secret as long as may be considered necessary. In other cases there may be no objection to commercial user of the invention being authorised either during or after the end of the war.

5. It is obviously important that the State should have the power of exercising some control over these cases. At the same time, it is clear that those who render valuable assistance should not be left without a fair reward for their work.

6. Each case must necessarily be dealt with on its merits, and it is difficult, and perhaps undesirable, to prescribe rigid rules in such a matter, but it seems necessary, nevertheless, to lay down a few general principles, and My Lords suggest the following as appropriate for Admiralty transactions:—

- (1). No patent to be applied for without prior Admiralty concurrence.
- (2). If the Admiralty considers that the invention ought, in the national interests, to be kept permanently secret, then a Secret Patent is to be applied for at Admiralty expense in the name of the inventor or inventors (including when applicable the name of any scientific body that may in its corporate capacity have contributed to the evolution of the invention) coupled with the name of any naval or Admiralty officer who may have contributed any substantial part to the evolution of the invention, and also with the Lords Commissioners of the Admiralty (or an officer representing them) in any case where they may so decide. The invention and patent to be assigned permanently to the Admiralty and sealed as secret, as provided in the Patent Act, the inventor or inventors undertaking to keep it secret.
- (3). If the Admiralty wish the invention kept secret during the war, but not longer, then an ordinary patent to be applied for, at the Admiralty expense, in name or names as under (2), if the inventor or inventors so desire. The patent is not to be assigned to the Admiralty or sealed as secret, but publication to be prohibited during the war under Section 18 B of the Defence of the Realm Regulations, except that, if so agreed by the Admiralty, patents can be applied for in allied countries and British Dominions, subject to secrecy during the war.
- (4). If the Admiralty do not consider it necessary to keep the invention secret at all, then an ordinary patent in the name or names as under (2) can be applied for, the expense being borne by the inventor or inventors, unless the Admiralty decides to join in the patent and to pay the expense.

- (5). The amount of remuneration to the outside expert or scientific body concerned for assignment of patent under (2), or for any use that may be made in His Majesty's Service of patents under (2), (3), or (4), as well as the amount of remuneration to any Admiralty or naval officer joined in the patent, is to be considered by the Ordnance Council (or by the Admiralty members of the Ordnance Council in the case of an invention which is of interest to the Naval Service only) assisted in these cases by independent representatives from outside the service possessed of scientific and commercial knowledge. Their award to be subject to the approval of the Treasury.
- (6). In settling the amount of any award under Paragraph (5) due consideration to be given to the extent of assistance or facilities afforded by the Admiralty, or enjoyed by any naval or Admiralty officer concerned as a result of his position and experience gained in the service. In cases where the Admiralty has afforded assistance or facilities, the Department would have the right to share *pro tanto* in any commercial profits derivable from the invention. If the Admiralty decides not to make any such claim, the value of such commercial profits as the Admiralty might reasonably have expected to obtain will be taken into account in settling the terms to be paid for use of the invention in the service. Conversely, where the invention is capable of commercial application, but is dealt with under Paragraph (2), the terms shall take into account the value of any commercial profit which the inventor may have been deprived of by publication having been prohibited.
- (7). Any licences, &c., granted by the patentees in cases (3) and (4) to other parties to be referred to the Admiralty beforehand, and to contain provisions approved by the Admiralty safeguarding the right of the Admiralty to use the invention on terms to be settled as under (5).
- (8). If publication of the results of any research is prohibited for reasons of state, the Admiralty will be prepared to consider the question of issuing some form of official announcement in the press, giving due credit to the individual or individuals concerned in cases where the publication of the results (if permitted) might have enhanced his or their reputation in the scientific world.

THE FOOD ECONOMY CAMPAIGN.

IN preparation for the Food Economy Campaign which the War Savings Committees are about to undertake all over the country, the whole press, and especially the scientific press, ought to lose no opportunity of emphasising the importance of the serious consideration of the food problem.

The Editor of this journal was the first to call the attention of the public to the question of our wheat supply, and many years ago he urged the necessity of approaching the problem from a scientific point of view, to avoid the errors into which haphazard and ill-considered methods would lead us. The catastrophe which could not then be foreseen has come upon us, and the time for warnings and discussions is past; the need for organised and decisive action is pressing, and it may indeed be truly said that the crisis is upon us, and will have to be faced within the next few months or perhaps weeks. The impending very serious shortage of food must be met sanely and rationally.

If we examine the facts before proceeding to suggest remedial action, we shall find that, on the best authority, it may be asserted that a time of great deficiency in the wheat supply in England is at hand, owing partly to the depredations of the U-boats. Moreover, a world shortage

is imminent, caused by the lack of labour, by the poorness of recent crops, and by other circumstances. The deficiency in the world's wheat crop for 1916-17 amounts to 25 per cent of the average, and the other cereals show a similar deficiency, except oats, of which there appears to be an appreciable surplus. The aggregate yield of the five cereals—wheat, rye, barley, oats, and maize—is only about 80 per cent of that of 1915, and about 88 per cent of the average of the preceding five years. Hence distress and even famine are within measurable distance, although it is difficult to make the public regard the last statement as a fact and not merely as a vague prophecy which is not in the least likely to be realised, and to take it with seriousness. Clearly the remedy, and the only remedy, is the reduction of our consumption of bread and bread stuffs. If the quantity consumed per head of the population were lowered by 1 lb. per week below the normal there would be no fear of distress to anybody. The adoption of a scheme of compulsory rationing is undoubtedly not the best way to effect this reduction, although the authorities will be obliged to fall back upon it if reason and argument fail to evoke the voluntary response of the nation. Compulsion has been found to be an unwieldy implement, which works unjustly and harshly and brings in its train many abuses. It is obvious that the young and the aged, the idle, and the workers have very different requirements in the way of food, and the allowance of bread necessary for different classes of workers must vary between very wide limits if there is to be anything like equality of sacrifice for all. The agricultural labourer requires a great deal more than the clerk, and those who can afford more meat can do with less bread. Again, it is specially incumbent upon those who can afford the additional expense of the greater amount of cooking required to make the most use of the available substitutes for bread—oat, barley, and maize flour, and rice, &c.—and thus to bring their consumption considerably below the average of 4 lbs. of bread per week per person. There is urgent necessity for economy in all foods, especially in wheat products, and no opportunity must be lost of sounding the call for that reasoned and deliberate personal sacrifice on the part of every individual without which victory will inevitably be delayed.

THE ASSOCIATION OF SCIENCE, LIMITED.

ALL who are interested in science, or who wish to promote it, are invited to become members of this Association. Women as well as men are eligible as members.

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The management of the Association is in the hands of a Council elected annually by the members. The annual subscription is six shillings, payable in advance, and the further liability of members is limited to five shillings, payable only in the event of the Association being wound up.

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PROCEEDINGS OF SOCIETIES.

ROYAL INSTITUTION.

Annual Meeting, May 1, 1917.

THE DUKE OF NORTHUMBERLAND, K.G., President,
in the Chair.

THE Annual Report of the Committee of Visitors for the year 1916, testifying to the continued prosperity and efficient management of the Institution, was read and adopted.

The Report of the Davy-Faraday Research Laboratory Committee was read.

Twenty-three new Members were elected in 1916. Sixty-two Lectures and nineteen Evening Discourses were delivered in 1916. The books and pamphlets presented amounted to about 316 volumes, making, with 540 volumes (including periodicals bound) purchased by the Managers, a total of 856 volumes added to the Library in the year.

Thanks were voted to the President, Treasurer, and Secretary, to the Committees of Managers and Visitors, and to the Professors, for their valuable services to the Institution during the past year.

The following gentlemen were unanimously elected as Officers for the ensuing year:—

President—The Duke of Northumberland.

Treasurer—Sir James Crichton-Browne.

Secretary—Colonel Edmond H. Hills.

Managers—Henry E. Armstrong; Sir William Phipson Beale, Bart.; Charles Vernon Boys; J. H. Balfour Browne; John Y. Buchanan; W. A. B. Burdett-Coutts; Sir James Mackenzie Davidson; Donald W. C. Hood; The Rt. Hon. Viscount Iveagh; Sir Charles Nicholson, Bart.; The Hon. Richard Clere Parsons; Sir James Reid, Bart.; Alexander Siemens; Samuel West; The Rt. Hon. Lord Wrenbury.

Visitors—Ernest Clarke; John F. Deacon; Edward Dent; Lieut.-Col. Henry E. Gaultier; James Dundas Grant; W. B. Gibbs; W. A. T. Hallows; Henry E. Jones; H. R. Kempe; Francis Legge; James Love; Richard Pearce; Sir Alexander Pedler; Hugh Munro Ross; Joseph Shaw.

CORRESPONDENCE.

SULPHATE OF AMMONIA ASSOCIATION.

To the Editor of the Chemical News.

SIR,—We have pleasure in enclosing circular letter on the position of sulphate of ammonia.—I am, &c.,

SECRETARY,
Sulphate of Ammonia Association.

84, Horseferry Road, Westminster,
London, S.W. 1, April 16, 1917.

SIR,—Referring to our printed letter of February 12th and our subsequent letter enclosing a copy of the Equalisation Scheme, we wish to put before you a short statement of the present position.

The delivered price of £16 per ton and the altered conditions of sale for sulphate of ammonia for agricultural purposes were announced to the Sulphate of Ammonia Advisory Committee on February 10th as a decision of the War Cabinet.

In March the authorities of the Food Production Department of the Board of Agriculture took over from the Ministry of Food the regulation of sales and distribution of sulphate of ammonia, and on March 10th they

intimated to the Committee that, in their opinion, the method first proposed for meeting the delivery charges required reconsideration.

In the meantime, although a considerable number of the largest makers, most of whom would have been contributors rather than recipients of monies, had signed the Equalisation Scheme, only a meagre response to the invitation to become parties to the scheme was received from those makers for whose benefit the scheme was primarily intended.

The increase in home consumption this season has been enormous, and in view of the guarantee given to farmers by the Government in respect of prices for cereals and potatoes, it is anticipated that the agricultural demand for sulphate of ammonia next season will be far larger still; at the same time, the requirements of the Ministry of Munitions will, we understand, be very considerably greater in the near future than they have been hitherto; so that the Committee are of opinion that the total quantity of sulphate of ammonia available for export between now and the end of May, 1918, will not be sufficiently large to justify their asking makers to undertake the accounting and clerical work demanded by the Equalisation Scheme.

In view of these facts, the Committee have decided to withdraw the Equalisation Scheme, and are returning the forms to those makers who have already signed it.

In order to give effect to the decision of the War Cabinet that farmers are to be able to purchase sulphate of ammonia at £16 per ton delivered, we have agreed with the Food Production Department to recommend to makers for this season an arrangement by which that Department guarantees that in respect of deliveries made on or after February 12, 1917, up to and including May 31, 1917, for home agricultural use at not exceeding £16 per ton to farmers, or £15 10s. per ton to merchants delivered at any station in sellers' bags net cash, basis 24½ per cent ammonia, the Government will defray the whole cost of delivery, but makers will be called upon to credit the Government with 10s. per ton out of the price obtained from the buyers.

The Government will immediately create a Sulphate of Ammonia Fund, and will pay and collect monies directly to and from makers in respect of delivery charges.

The effect of this arrangement will be to guarantee that makers will receive a known definite price, viz., £15 10s. for sales to farmers or £15 for sales to merchants, free on rails at maker's works, 24½ per cent basis, in single bags, net cash.

A formal announcement of the details of the above arrangement will shortly be made to you by the Food Production Department.

With regard to the arrangements to be made for the season, June 1, 1917, to May 31, 1918, the Committee are now conferring with the Food Production Department as to the best means of supplying the demand for sulphate of ammonia.—Yours faithfully, D. MILNE WATSON, Chairman, Sulphate of Ammonia Advisory Committee.

Society of Chemical Industry.—The Annual General Meeting of the London Section will be held at Lyons' Birkbeck Café on Monday, May 7, at 8 p.m. The election of Officers and Committee for next Session will take place. The Chairman will give a brief report of the work of the Session. After the formal business has been taken, the meeting will resolve itself into an informal one. Mr. F. A. Hocking, of the Russian Government Committee, has promised to give a brief description of the chemical, medical, and sanitary war work organised by the Union of Zemstvos in Russia. Members who have travelled in Russia, or are in other ways interested in Russian affairs, are specially invited to attend.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clxiv., No. 10, March 5, 1917.

This number contain no chemical matter.

No. 11, March 12.

Determination of Ozone.—M. David.—The author has found that pure iron-ammonium sulphate in very dilute sulphuric solution is not oxidised in the air, but absorbs ozone more rapidly than any other substance. Thus ozone can be determined by allowing a solution of iron-ammonium sulphate to absorb it and then titrating directly with potassium permanganate. To prepare the liquids, 3.920 grms. of the sulphate are dissolved in distilled water to which 20 cc. of pure sulphuric acid at 66° are added and the solution is made up to 1 litre at 15°, and 0.316 gm. of crystallised pure permanganate is dissolved in distilled water and the solution made up to 1 litre at 15°.

No. 12, March 19.

This number contains no chemical matter.

No. 13, March 26.

Biochemical Synthesis with the Aid of Emulsin of a Second Galactobiose.—Em. Bourquelot and A. Aubry.—When the residues from the preparation of the galactobiose already described were worked up a second isomeric galactobiose was isolated. It crystallises in microscopic needles and has only a slightly sweet taste, recalling that of milk sugar. It is dextrorotatory and possesses multi-rotation. Like the previous galactobiose, it is a reducer.

No. 14, April 2.

New Dyes for Microscopy derived from Methylene Blue.—L. Tubondeau and J. Dubreuil.—In order to prepare methylene azure and methylene violet, the authors boil together ammonia and methylene blue, when an abundant precipitate is formed. On evaporating the filtrate and drying practically pure methylene violet is obtained. The precipitate gradually changes colour on exposure to the air, becoming blue-black. It is then taken up with water, filtered, and the filtrate treated as above. The powder thus obtained is methylene azure. These two powders can be used for the preparation of—(1) An aqueous solution of azure; (2) an aqueous solution of azure and violet, which the authors call ammoniacal polychrome blue; (3) an alcoholic glycerine solution of azure and eosine, analogous to Giemsa mixture, which they call "azeo." The first is made by dissolving 1 gm. of the ammoniacal azure in 100 cc. of distilled water; the second is a mixture of 1 per cent solutions of azure and ammoniacal violet; while azeo is made by mixing solutions of ammoniacal azure and eosine in 75 parts of ethyl alcohol and 25 parts of glycerine. Azeo can be employed like Giemsa mixture.

Bulletin de la Société Chimique de France.
Vol. xxi.-xxii., No. 2, 1917.

Loss in Alcoholic Fermentation.—L. Lindet.—Saccharose is a bad food for yeast, and in its presence ammonium salts are only very slowly transformed into proteins. This is no longer the case when more assimilable carbohydrates are added to the sugar. The synthesis of proteins then becomes as rapid and easy as if an already formed protein were supplied to the yeast. The loss per unit of yeast recovered can be used to measure the value of the foods provided for the yeast.

MISCELLANEOUS.

The Biochemical Society.—The next meeting of the Society will be held in the Cancer Hospital, Research Institute, Brompton Road, London, S.W., on Monday, May 14, at 5.30 p.m.

Studies of Solution—I. The Change of Molecular Solution Volumes in Solutions. II. A Conception of Osmotic Pressure.—Shinkichi Horiba.—The author describes a method of determining the molecular solution volumes of solute and solvent in solution, and gives the results of determinations of molecular solution volumes of cane-sugar, potassium, sodium, ammonium, and lithium chlorides in aqueous solutions at various temperatures. Some relations between the molecular volume of a solute and its solubility have been pointed out, and a theory regarding the state of solution has been suggested. According to this theory the molecular solution volume of a solute increases with the concentration, while the molecular solution volume of the solvent decreases as the concentration increases. When the molecular solution volume of the solute reaches a certain definite value the solution becomes saturated, and this molecular solution volume in the saturated solution is almost equal to the molecular volume of the solute in a pure state. As regards the explanation of osmotic pressure, the author believes that the analogy between the gaseous state and solution is questionable, and he holds the same view as Ehrenfest with respect to osmotic pressure, *i.e.*, that osmotic pressure is not caused by the bombardment on a semi-permeable membrane of the molecules of the solute, but by the penetration of the water through the membrane, giving rise to a hydrostatic pressure which prevents the further passage of the water.

Queensland Eucalyptus Trees and Malaria.—During the later decades of the nineteenth century it was a common practice to plant Australian blue-gum or eucalyptus trees in districts all over the civilised world infected by malaria fever. It was held that the essential oil produced by the leaves combated the harmful vapours rising from the swamps laden with the poison of the disease. The discovery that the malarial germ is introduced into the blood by a mosquito has settled once and for all the origin of the disease. Yet it is only within the last few months, writes our American correspondent, that a somewhat mysterious point has been fully settled. The theory that the eucalyptus trees neutralised the poison vapours is nonsense; yet the fact remains that where blue-gums were freely planted there was always a notable decline in the amount of malaria. For instance, in a certain district near Algiers the placing out of thousands of eucalyptus trees from Queensland completely transformed the conditions. Malarial fever, of a peculiarly virulent type, had formerly been a constant feature, but within twelve months of the planting of the blue-gums the disease entirely disappeared, and is now unknown. What is the explanation of this circumstance? It has been demonstrated that, of nearly all trees, the eucalyptus absorbs the greatest amount of water. Seeing that blue-gums increase in height with great rapidity, often growing many inches a day in a hot position, the amount of moisture taken up increases on a greatly progressive scale; and this is just what brings about the downfall of the malarial mosquito. To complete its life-cycle it is necessary that this insect should pass its larval stage in pools of water. With the coming of the eucalypti these pools and, indeed, all marshy places disappear; the breeding spots of the mosquitos are gone, and in time the insects vanish altogether. The district is then free from malarial trouble simply because the carriers of the disease are not able to keep going. Still, we owe to Australia this great discovery.—London Correspondent of the *North Queensland Register*, Weavers' Hall, 22, Basinghall Street, London, E.C. 2.

MEETINGS FOR THE WEEK.

- MONDAY, 7th.—Royal Society of Arts, 4.30. (Howard Lectures). "The National Shortage of Iron Ore Supplies," by Prof. W. G. Fearnside.
Society of Chemical Industry, 8. (Annual General Meeting).
Royal Institution, 5. (General Meeting).
TUESDAY, 8th.—Royal Institution, 3. "Rhythmic Action in Muscle and in Nerve," by Prof. C. S. Sherrington.
WEDNESDAY, 9th.—Royal Society of Arts, 4.30. "Works Organisation and Efficiency," by Prof. W. Ripper.
THURSDAY, 10th.—Royal Institution, 3. "Pagan Religion at the Time of the Coming of Christianity—Dea Roma, The Mystery Religions, Philosophy, Conclusion," by Prof. Gilbert Murray.
Royal Society. "Permanent Periodicity in Sun-spots," by Sir Joseph Larmor and N. Yamaga. "The High-frequency Resistance of Multiply-stranded Insulated Wire," by Prof. G. W. O. Howe.
FRIDAY, 11th.—Royal Institution, 5.30. "Radio-active Haloes," by Prof. J. Joly.
SATURDAY, 12th.—Royal Institution, 3. "The Electrical Properties of Gases," by Prof. Sir J. J. Thomson, O.M.

TO comply with Regulation 8 (b) of the Defence of the Realm Act, advertisements from firms whose business consists wholly or mainly in Engineering, Shipbuilding, or the production of Munitions of War, or of substances required for the production thereof, must include the words "No person resident more than ten miles away or already engaged on Government work will be engaged."

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Wanted, "MEMOIRS OF THE GOODWIN SANDS," by Mr. Gattie.—Address, W. S., CHEMICAL NEWS Office, 16, Newcastle Street, Farringdon Street, London, E.C. 4.

TO BE SOLD.

"Journal of the Society of Chemical Industry"—1885 to 1916.
"Chemisches Zentralblatt"—1913, Vols. I. and II.; 1914, Vol. I. (Complete). Also, 1913, Vols. I. and II.; 1914, Vols. I. and II.; 1915, Vol. II. (Odd numbers, the series not quite complete).

WANTED.

"Berichte"—1914, September to December, Nos. 13 to 19; 1915, No. 7; 1916, No. 13.
"Chemisches Zentralblatt"—1915, Vol. II., Nos. 20, 21; 1916, Vol. I., Nos. 1, 2, 3, and Vol. II., Nos. 1, 2, 3, 4.
"Farber-Zeitung"—1914, Nos. 15, 16, 17, 18, 22; 1915, Nos. 10, 11, 12, 19.
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THE CHEMICAL NEWS

VOL. CXV., No. 2998.

FISCHER'S SYNTHESIS OF DEPSIDES AND TANNING SUBSTANCES.*

By Prof. J. A. WILKINSON, M.A., F.C.S.

(Concluded from p. 209).

UNDER the generic name of tannin, a large number of vegetable substances from different sources have been included, which have been classified at various times in various ways, according to the point of view chosen. The experiments undertaken in this case were limited to the tannins of gall apples and some substances which belong to the same type. The first experiments carried out by Fischer and Freudenberg had for their object the question whether the glucose, first observed by Strecker in 1852-4, was in reality a component of the tannin molecule or merely an accidental adulteration. For this purpose they used as raw materials:—

(a) *Acidum tannicum leviss. furiss.* (Merck's purest preparation); (b) ditto (Kahlbaum), both of which they subjected to purification by special methods devised for this purpose. Briefly these consisted in: (1) Extraction with ether, which gave a yield of 60 per cent; (2) extraction with ethyl acetate gave a yield of 60 per cent; (3) preparation of the potassium salt and subsequent acidification with $\text{N.H}_2\text{SO}_4\text{Aq}$.

The object was to get a preparation as pure as it was possible to get. The purified tannin so prepared was so hygroscopic that great care had to be taken to exclude the moisture of the atmosphere when weighing. On analysis the following numbers were obtained:—

	Carbon, per cent.	Hydrogen, per cent.
I. Merck's tannin purified by Method 2	53.3	3.25
II. Kahlbaum's " "	53.7	3.3
III. Kahlbaum's tannin purified by Method 3. " " " "	53.62	3.39
IV. Kahlbaum's tannin, not purified, but dissolved out with water " "	53.16	3.4
V. Merck's tannin purified by Method 1	52.59	3.24

The optical rotatory power was also determined, and gave for three different preparations of I. the values—

$$[\alpha]_{\text{D}}^{20} = +67.65^\circ (\pm 2^\circ); \text{aqueous solutions.} \\ +70.09^\circ (\pm 1^\circ). \\ +18.43^\circ (\pm 3^\circ); \text{alcoholic solution.}$$

For two different preparations of III. the values—

$$[\alpha]_{\text{D}}^{20} +70.77^\circ (\pm 2^\circ); \text{aqueous solutions.} \\ +68.48^\circ (\pm 2^\circ).$$

And for V.—

$$+58.23^\circ (\pm 2^\circ).$$

Theoretically—

	C, per cent.	H, per cent.
Digallic acid contains..	52.16	3.13
Pentagalloyl glucose ..	52.33	3.13
Pentadigalloyl glucose .	53.63	3.08

These analyses did not lead to any definite conclusion. The acidity was next tested and found to be one-tenth that of gallic acid.

Hydrolysis was then undertaken with dilute sulphuric acid in order to separate the sugar, which was very care-

fully estimated by several methods, from the acid portion of the molecule. Examination and analysis of the osazone proved conclusively that dextrose was present and the acid gallic acid. If the hydrolysis were not completed, in addition to the gallic acid and glucose, a dark coloured substance remained, which was called the tannin residue. As a final check, artificial mixtures of gallic acid and dextrose were also made and similarly treated. The acid used was 5 per cent $\text{H}_2\text{SO}_4\text{Aq}$, but in one case, Strecker's method, using 11 per cent $\text{H}_2\text{SO}_4\text{Aq}$ and heating for twenty-four hours at 100° was employed. The results obtained are shown in Table A.

These experiments lead to the conclusion that in the purest tannin investigated 1 mol. glucose is combined with about 10 mols. gallic acid, and no other phenol-carboxylic acid is present. In order to elucidate its structure still further, an attempt was made to isolate intermediate products, but this was found to be impossible owing to their properties, in consequence of which the synthetic method was adopted. No free carboxyl being present, as the above experiments showed, the method of combination of the glucose with the gallic acid was indicated as being in the form of an ester, and these conditions are satisfied if tannin be considered as a compound formed by the union of 1 mol. glucose with 5 mols. digallic acid, similar to pentacetylglucose. Digallic acid, $\text{C}_6\text{H}_2(\text{OH})_2\text{COOC}_6\text{H}_2(\text{OH})_2\text{COOH}$, is a depside, which was synthetically prepared in a pure condition, first by Fischer in the manner indicated above, but, as it is extremely difficult to work with, an attempt was first made with gallic acid in order to obtain pentagalloyl glucose, $\text{C}_6\text{H}_7\text{O}_6\text{OC}_6\text{H}_2(\text{OH})_3$, and test its properties.

The methods hitherto used for the complete acylation of glucose were found to be unavailable for the preparation of pentagalloyl glucose, and a new method had to be worked out. This was done, and consisted in bringing together the glucose and the chloride of the acid dissolved in dry chloroform, together with quinoline. In this manner pentatrimethylcarbonatogalloyl glucose (mol. wt. 1870.5), $\text{C}_{71}\text{H}_{62}\text{O}_{56}$ or $\text{C}_6\text{H}_7\text{O}_6\text{OC}_6\text{H}_2(\text{OCOOCH}_3)_3$, was obtained as a granular colourless amorphous powder sintering about 90° , $[\alpha]_{\text{D}}^{20} +34.34^\circ (\pm 0.4^\circ)$. By careful saponification with excess alkali in aqueous acetone solution at ordinary temperature this yielded pentagalloyl glucose, $\text{C}_{41}\text{H}_{32}\text{O}_{26}$ (mol. wt. 910.26) as a yellow amorphous powder, softening about 150° and beginning to decompose at 160° , $[\alpha]_{\text{D}}^{20} +31.35^\circ$.

This substance shows a startling similarity to tannin, the chief differences being the optical rotation and the amount of gallic acid obtained on hydrolysis with sulphuric acid. It possesses a strong astringent and bitter, but not acid, taste. It is soluble in most of the organic solvents, gives coloration with ferric chloride (inks), and is precipitated by the same reagents. Analysis gave—

Carbon, per cent ..	52.49	Hydrogen ..	3.79
	52.41		3.67
Theoretical	52.33		3.43

The benzoylation of glucose was also carried out, and in this case two stereoisomers were obtained which could be separated by crystallisation, according as α - or β -glucose was used, but in the case of the corresponding galloyl compounds, owing to their amorphous nature, this was impossible. From analogy and other considerations Prof. Fischer does not consider that the pentagalloyl glucose is a single uniform substance, but probably a mixture of isomers.

In spite of this, he states that with its preparation the chapter of the principal synthesis seems to be concluded, though not yet fully completed, owing to the fact that tannin itself has not yet been synthesised. A large number of other experiments have been carried out, some dealing with other commercial tannins, which were purified and hydrolysed as above, others being attempts at synthesis along the above lines, but these have not yielded

* From the South African Journal of Science, xiii., No. 4.

TABLE A.

Material.	Duration of hydrolysis.	Gallic acid dried.	Tannin residue.	Glucose (per cent).				Total.
				Polar.	Fehling.	Grav.	Average.	
Tannic acid	5	—	—	—	—	0.5	0.5	—
	20	—	—	—	—	1.1	1.1	—
	24	80.2	13	1.3	2.2	2.5	2.0	95.2
	45	90.4	3.9	4.0	3.8	4.7	4.4	98.7
Tannic acid—Kahlbaum .. .	60	88.7	1.5	5.8	6.9	7.6	6.8	97.0
	72	93.7	1.5	7.3	7.5	9.0	7.9	103.1
	87	90.9	—	5.0	6.4	7.9	6.4	97.3
	8	—	—	—	—	2.6	2.6	—
Tannic acid—Merck .. .	24	87.2	—	—	—	4.9	4.9	—
	72	94	1	5.3	7.4	8.3	7.0	102
Tannic acid—Merck, purified by Method 1	8	—	—	3	4	—	3.5	—
Tannic acid—Merck, purified by Method 2	18	72.7	22.2	—	—	3.2	3.2	98.1
	72	93.6	—	5.9	6.0	8.4	6.8	100.4
Tannic acid—Kahlbaum, purified by Method 2 .. .	24	81.2	18	3.1	3.1	3.3	3.2	102.4
Tannic acid—Kahlbaum, purified by Method 3 .. .	51	92.1	3.8	7.5	6.8	7.6	7.3	103.2
Tannic acid—Kahlbaum, purified by Strecker's method .. .	24	94.3	—	4.6	6.8	7.3	6.2	100.5
Mixtures—								
95.2 per cent water-free gallic acid, 4.8 per cent glucose .. .	24	90.2	—	—	—	3.7	3.7	93.9
91.8 per cent water-free gallic acid, 8.2 per cent glucose .. .	30	86.8	1.3	4.0	3.8	5.1	4.3	92.4
86.6 per cent water free gallic acid, 13.4 per cent glucose .. .	30	85.0	—	7.8	9.1	10.3	9.1	91.1

the results expected. Nor has anything occurred which has yielded such strong evidence of the structure of the tannin molecule as the synthesis of pentagallicol glucose.

Other pentacyclated glucoses have also been prepared, namely, the parahydroxybenzoic, salicylic, and pyrogallol-carboxylic acids, also probably mixtures of the α - and β -stereoisomers.

The bearing of the above syntheses on the chemical processes occurring in plants is of extreme interest, as showing that the polyvalent alcohols can be utilised by the plant in the esterification of acids, the free acids themselves being found only in a few species, and the significance of this is of the utmost importance to vegetable physiology as the sugar derivatives found so widely distributed have not hitherto been regarded in this light.

The compounds of high molecular weight and known constitution prepared in the course of these researches are also of great interest from a theoretical point of view.

The above résumé has been prepared from the various papers by Fischer and his pupils published in the *Berichte*. For other work dependence has been placed upon abstracts.

within the circle is to be multiplied to obtain the number of grains per square mm.

TABLE VI.

Magnification used.	Diameter of circle. Mm.	Factor.
25	79.8	$\frac{1}{2}$
50	79.8	$\frac{1}{4}$
100	79.8	2.0
150	79.8	4.5
200	79.8	8.0
250	79.8	12.5
500	79.8	50.0
750	79.8	112.5
1000	79.8	200.0
1500	79.8	450.0
2000	79.8	800.0

The following example shows how this table is used:—Included grains, 61; boundary grains, 35; magnification, 100. Grains per square mm. = $[61 + (0.6 \times 35)] 2 = 164$. Similar tables can be made for square inch calculations or for circles of different diameters.

Apparatus and Manipulation for Grain Size Measurements.

Any good metallurgical microscope with camera attachment can be used for grain size determinations. It is recommended that only even magnifications be used. For instance, if an observation is being made at a magnification of 460 diameters, the setting should be changed to 500 diameters.

Grain size measurements can be made on a screen or on a photograph. Either a ground-glass or a piece of paper fastened to a clear glass may be used as a screen. A convenient system, where records of the determinations are kept, is to cut several pieces of thin typewriter paper so that they fit the clear glass screen, and draw a circle with the desired diameter near the centre of each sheet. Fasten one of these pieces of paper to the clear glass screen by

GRAIN SIZE MEASUREMENTS IN METALS, AND IMPORTANCE OF SUCH INFORMATION.*

By ZAY JEFFRIES, B.Sc., Met.E.,
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(Concluded from p. 207).

Quick Method of Grain Size Measurement by the Author's Method.

A QUICK way to make a grain size determination by this method has been developed. A circle 79.8 mm. in diameter is used. In making a grain size determination, one of the magnifications given in Table VI. is used. In the third column is given the factor for each magnification, by which the equivalent number of whole grains

* A Paper read before the Faraday Society, May 9, 1916.

means of gummed labels, or otherwise, and project on to it the image of the specimen.

The circumference of the circle should be well within the image. Count and check separately the boundary grains and the included grains, make calculation for grains per unit area, and save the sheet of paper with check marks and calculations. This will serve as a permanent record of the determinations.

If the existence of a grain boundary is doubtful, often a slight change of focus will remove the doubt. It is therefore essential that the fine focusing screw be provided with an extension, so the focus can be changed while the operator examines the image on the screen.

Unless the room is rather dark, or the microscope lamp very strong, the operator will find it helpful to work under a cloth hood.

The specimen should be etched so as to bring out distinctly the grain or cell boundaries.

It has been found more satisfactory to make grain size measurements on a ground glass or paper screen than on photographs, for the reason that it is often hard to properly distinguish between adjacent grains in photographs, while a slight change of focus when examining the image of the metal itself will often remove any doubt.

Mathewson and Phillips (*Bull. A.I.M.E.*, January, 1916, 33) apply Heyn's method for grain size determinations in the following manner:—

"Five parallel equidistant lines are ruled in one direction, and five in a direction at right angles to this upon a clear gelatine-coated glass plate. This plate is then placed upon the photomicrograph and counts made along the lines for a uniform distance of 2.75 in. From the five counts in each direction the average number of grains per inch in each direction is calculated."

Sampling.

Since some metallographic specimens have several million grains exposed on one face the problem presents itself to obtain a representative sample of this face. The following rules are offered with the idea that they may be helpful:—

1. Use such a magnification that about 50 grains will be included within the circle. It is better to have more than 50 grains included within the circle than less, but is always recommended that an even number of magnifications be used, even though the number of included grains should exceed 100.

2. Make at least five determinations at about equal intervals along a diameter of the specimen. The average of all of the determinations is taken as the final result. It is evident that if there is much difference in grain size between the edge and centre of the specimen, the former should have the greater weight. Such a case, however, may come under Rule 4.

3. If the samples are small enough (for example, small wire) it is advisable to determine the total number of grains on transverse sections, and the total number for a given length on longitudinal sections. It is sometimes practicable to do this with larger coarse-grained specimens, either macroscopically or at low magnifications.

4. When one part of a specimen differs greatly from another part in grain size do not average the separate determinations, but record each and note the position of each determination by means of a freehand sketch.

5. In samples which have been cold worked the relative degree of cold work in any direction is expressed by the ratio of the length divided by the width of the grains. The actual amount of cold work in any direction is the ratio of the average dimension of the grains in that direction divided by the average diameter of the grains in the metal before working. If this ratio is less than 1, the grains in this dimension have been compressed; and if greater than 1, the grains have been stretched. For obtaining these ratios it is recommended that Heyn's method be used.

Interpretation of Results.

Distinction should be made between grain and cell. Any of the above methods may be used to determine cell size; for example, in steel, as well as the grain size in commercially pure metals, solid solutions, and alloys consisting largely of one component. However, with an alloy such as steel, where a network is encountered, the term "cell" should be used.

When a cold worked metal has been annealed and recrystallisation has taken place, the resulting grains are not exactly equi-axed, but are usually longer in the direction of original deformation. From the grain size measurements it would be difficult in some cases to tell whether this persistent elongation of the grains was the result of moderate cold work without annealing or excessive cold work followed by annealing. However, the specimen usually furnishes a clue which will answer this question. If the elongation of the grains is due to a moderate amount of cold work without annealing, elongation of the individual grains will be the greater in the neighbourhood of the points of application of the deformational forces; for example, in rolling, drawing, or hammering, the deformation of the individual grains will be greater near the surface than at the centre. In metals which have been excessively cold worked and have undergone recrystallisation by annealing this difference is not marked.

H. Baucke ("On Some Recent Microscopical Investigations of Copper," International Association for Testing Materials, Sixth Congress, New York, 1912) finds that in copper which has been severely cold worked and annealed at various temperatures the resulting recrystallised grains are longer in the direction of deformation until an annealing temperature of 900° C. is reached. If the annealing temperature is above 900° C. the grains are longer in the direction perpendicular to that of deformation. From the writer's experience it would seem that such a condition is not general in metals; in fact, there seems to be a great tendency for recrystallised grains, after severe cold working, to have their longest dimension in the direction of deformation, even after a long sojourn at relatively high temperatures.

Elongated grains which are not due to cold work are encountered in other places; for example, cast metals which have solidified progressively from the shell of the retaining vessel toward the interior of the mass of metal will have elongated grains, depending upon the direction of cooling.

Stead and Carpenter report this condition in the case of pure iron when cooled from above the upper critical temperature ("The Crystallising Properties of Electrodeposited Iron," *J.I.S. Inst.*, No. 2, 1913, 119). By controlling the direction of cooling elongated grains can be produced with the length several times the width. In such cases these elongated grains have physical properties more like equi-axed than cold worked grains. This is no doubt due to the fact that the cold worked grains contain amorphous metal all through the mass, while the amorphous metal of elongated grains which have formed during the regular process of grain growth will be at the boundaries only.

Grains of various shapes can also be produced by controlling the direction of heating cold worked metals.

Except in these special cases elongated grains will indicate that the metal has been cold worked. In cold worked metals measurements parallel and perpendicular to the direction of working should show fairly constant ratios when determined by Heyn's method.

Metals which have been cold worked and subsequently annealed at temperatures well above the recrystallising range are apt to have very even grain size (F. Robin, *Journ. Phys.*, 1914, iv., 37).

As mentioned in the earlier part of this paper the only way in which the proper interpretation of grain size determinations can be made is to correlate these measurements with the physical properties, chemical composition, and the life of the metals in use.

THE ORGANIC NITROGEN COMPOUNDS OF
SOILS AND FERTILISERS.*

By ELBERT C. LATHROP, Ph.D.

Usual and Unusual Nitrogenous Soil Constituents.

HISTIDINE, hypoxanthine, cytosine, xanthine, nucleic acid, creatinine, cyanuric acid, or its isomer cyamelid, may then be considered to be organic nitrogenous constituents commonly occurring in soils.

Arginine, lysine, adenine, choline, trimethylamine may be considered at the present time to be nitrogenous constituents unusual to soils, inasmuch as they occur infrequently in soils. These compounds may either not be normally formed by the processes of change taking place in the soil, or if they are formed they are probably very quickly changed into other compounds; for example, arginine into ornithine and urea, or adenine into hypoxanthine. Regarding tetracarboximid and urea no statement can be made at present.

The Changes produced in the Nitrogenous Organic Matter of Soils by the Process of Partial Hydrolysis.

Having established the fact that a number of the simpler primary protein decomposition products are normally occurring soil constituents, likely to be found in all soils under agricultural occupation, it seemed desirable to see if it might not be possible also to demonstrate the presence in soils of compounds more complex than any of these. Two methods exist of determining this experimentally, first, directly by isolation of the complex compounds, and, second, by isolation of their component units, produced by treatment of the soil after previously establishing the absence of these units in the untreated soil. The second method is the one employed in this investigation.

The soil treatment used in decomposing these more complex nitrogen compounds was steaming. The effect which moist heat produces upon pure protein material is that of partial hydrolysis, the extent of the hydrolysis depending on the temperature reached and the length of treatment. The effect which heat has upon soils is a subject which has been, and is, rather prominently before agricultural investigators. It is a subject which has been receiving increasing attention, particularly from the point of view of sterilisation or partial sterilisation of the soil. Since heat activates the changes going on normally in soils, it is obvious that a study of heated soils also throws light upon the biochemical changes taking place in soils under field conditions.

Notwithstanding the fact that some of the results obtained by some of the investigators (see Note) on this subject are contradictory, especially in regard to the effects of steam sterilisation of soils on crops, they seem to warrant the following conclusions:—

By steam-heating the physical, chemical, and physiological properties of soils are more or less altered. The chemical changes consist in the increase in soluble matter in the heated soils. This is partially of an inorganic nature, potash and phosphoric acid being mainly determined, but the largest increase is in the organic matter rendered soluble. Ammonia is formed by the reduction of nitrates to nitrites and ammonia, but especially from the decomposition of organic matter. Large amounts of nitrogenous matter are made soluble and apparently more available for plant use, and carbon dioxide is produced in large quantities.

The nature of the chemical changes observed by these investigators is not made clear, although a number of suggestions, or hypotheses, have been put forward. These concern themselves partly with an explanation of the increase in mineral constituents, due to altered absorption

qualities for these constituents brought about by heat and by the greater hydrolysis or solubility of the minerals under the conditions of high temperature. Nearly all have particularly noticed the greater increase in soluble nitrogen, and coincident with this the increase in soluble organic matter. It is these latter observations which have been the source of most of the speculations to explain the increase and decrease, as the case may be, of plant growth on soils thus heated. These views are usually coupled with the biological idea which furnished the motive for the experiment.

In no case has any definite compound been obtained, either as an end or intermediary product of the changes brought about by the heat, and the subject is left in the same state of indefinite generalisations in which soil organic matter or humus found itself in the course of the past half century. In view of this lack of knowledge concerning the chemistry of soil organic matter itself, and its transformations under ordinary conditions, it is not to be expected that changes like the above could have been clearly defined.

The investigations of the past few years have brought with them an increasing knowledge of the nature of organic matter, especially with regard to the isolation and identification of specific chemical compounds from soil, so that the biochemical changes taking place in soil are becoming clear. In connection with these investigations methods for the recognition or isolation of specific chemical compounds have been developed. With such knowledge at hand, it seemed possible to go one step further and show the changes produced in soil organic matter in the process of sterilisation by heat, and thus be able to interpret these changes.

(NOTE.—In this connection see the following:—A. Baumann, 1887; Bolley, 1911; Darbishire and Russell, 1907; Deherain and Demousse, 1896; Dietrich, 1901; Fletcher, 1910; Frank, 1888; Hébert, 1889; Hiltner and Sörner, 1903; Hutchinson and Miller, 1911; Kasseroff, 1906; Kelly and McGeorg, 1913; Koch and Lücken, 1907; König, Hasenbaumer, and Copenrath, 1906, 1907; Laidlaw and Price, 1910; Lathrop, 1912; Lemmermann, Fischer, Kappen, and Blanck, 1909; Liebscher, 1893; Loew, 1909; Loew and Aso, 1907, i., ii.; Loges, 1886; Lyon and Bizzell, 1909, i., ii., and 1913; Peterson, 1911; Pfeiffer and Frank, 1896; Pfeiffer, Frank, Friedlander, and Ehrenberg, 1909; Pfeiffer, Guttermann, and Theile, 1910; Pickering, 1908, i., iii.; Richter, 1896; Rudd, 1893; Russell, 1910; Russell and Hutchinson, 1909; Russell and Petheridge, 1912, 1913; Schmoeger, 1893; Schreiner and Lathrop, 1912; Seaver, 1909; Seaver and Clark, 1910; Selby, 1896; Stone and Smith, 1901, 1902; Stone and Monahan, 1904; Stuart, 1905; Vogel, 1914; and Wilson, 1914).

The Soils Studied.

The soils used in this investigation are two types of the Coastal Plains Soil Province, known as Elkton silt loam and Sassafras silt loam. These two soils were collected from the same farm, about four miles east of Easton, Md., April, 1911. The samples taken were from several spots within a radius of 40 feet in each case, and were collected in adjoining fields within 150 yards of each other.

Although these soils have the same geological origin, they are rather widely different in physical and chemical characteristics and in fertility. The differentiation is apparently due to drainage conditions. While the two soils are very distinct in colour and in general agricultural value, the change from one to the other is frequently so gradual that it is difficult to draw a distinct boundary line. The samples taken are strictly typical of the types.

Analysis shows that these two soils contain practically the same amount of organic matter, the Elkton 2.25 per cent, and the Sassafras 2.24 per cent; the former contains 0.13 per cent of carbonates, expressed as carbon dioxide, and the latter only 0.03 per cent. The two soils are both acid to litmus-paper, the Sassafras soil being slightly the

* Contribution from the Laboratory of Soil Fertility Investigations, communicated by Dr. Oswald Schreiner, and published by permission of the Secretary of Agriculture. From the *Journal of the Franklin Institute*, clxxxiii., No. 3.

more acid of the two. In regard to their oxidising power and their catalysing power, that is their power to decompose hydrogen peroxide, they are both very weak, the Elkton showing none at all and the Sassafras only a little. They both contain practically the same percentage of total nitrogen. When the soils are boiled with hydrochloric acid and the different forms of nitrogen determined according to the method of Osborne and Haris (1903), the soils show only trifling differences. The results obtained by this method of analysis are presented in Table I.

TABLE I.—*Different Forms of Nitrogen in Elkton Silt Loam and Sassafras Silt Loam. Results Expressed in Per Cent of Total Nitrogen in Oven-dried Soil,*

Form of nitrogen.	Elkton.	Sassafras.
Per cent of total nitrogen in soils	0.0859	0.0869
Total N in solution	91.83	91.08
N insoluble in HCl.	8.17	8.92
N as NH_3	0.83	2.27
N as amides	12.06	12.45
N as melanin N	18.96	19.63
N as diamino acids	5.53	7.17
N as monoamino acids	54.45	49.56

From Table I. it is apparent that the only difference worthy of mention is the fact that the Sassafras soil contains slightly more ammonia than does the Elkton soil, but this is much too small to account for the differences in fertility. It is apparent from all of the analytical data that, in a general way, these two soils are very similar in their organic composition, and that no methods of analysis, excepting the actual isolation of the various definite organic compounds which compose the organic matter, will show wherein this difference in their organic composition lies.

The methods of farm practice have been identical with these soils, and each has received the same kind of debris, manures, plant residues, &c., which by processes of decay go to form the organic matter of soils. If therefore differences in the organic matter of these soils are shown to occur, they must be the result of different processes of decomposition in the soils.

The Method of Heating.

For the purpose of heating the soils an autoclave such as is in general use was employed. The autoclave is of copper, so constructed that it may be automatically kept at 30 pounds steam pressure for any given length of time. The soils were heated in one gallon stoneware jars placed in the autoclave in a metallic rack, the jars standing one above the other, the lower one being about 4 to 5 inches above the bottom of the autoclave. These jars held approximately 10 pounds of soil. The soils were heated at 30 pounds pressure for three hours at a temperature of about 135° C. The soils were treated with alkali just as soon as they had cooled to room temperature, so that only the changes caused by the immediate heating were under observation.

Method of Extraction.

Owing to the small amounts of organic matter in these soils and also to the fact that not all of this organic matter can be extracted, large amounts of soil were worked upon. Generally 40 to 50 pounds of soil, both heated and unheated, were extracted with 2 per cent sodium hydroxide solution. No attempt was made to study the humus precipitate. The chief interest in the work centred in the nitrogenous compounds, especially those rendered soluble by heating of the soil. Such compounds would appear chiefly in the alkaline extract, and later in the acid filtrate from the humus precipitate.

Experimental Results.

In harmony with the observations of other investigators the total amount of water soluble solids was increased by the heating. The soils by the bridge method showed the

following content of total soluble solids:—The normal Elkton soil, 184; the heated Elkton soil, 336; the normal Sassafras soil, 151; the heated Sassafras soil, 270 parts per million of dry soil. It will be noticed that the poorer soil, namely, the Elkton, showed the higher content in both heated and unheated condition. No further examination of the saline material was made.

By heating, the acidity of both soils was increased towards litmus-paper. It should be noted, however, that ammonia and amines were also formed in the process of heating, as was indicated by the fishy odour upon adding the alkali in the process of extraction. The results obtained in isolating and identifying the organic nitrogenous constituents extracted from the heated and unheated soils are concisely given in Table II.

The results in Table II. show only whether the organic compound was present or not. While no quantitative methods for the separation of these compounds from soils exist, owing to a great variety of difficulties which will not be discussed here, still in the work it was possible to distinguish between very small amounts and larger ones.

As seen from the table the nucleic acid was found in both soils, in the heated as well as in the unheated samples.

Xanthine was found in both the heated and unheated Elkton soil, but in larger quantity in the heated soil. In the case of the Sassafras soil it was found only after heating.

Hypoxanthine was not found in the Elkton soil, but after heating a small amount was obtained. The Sassafras soil contained this constituent, but its quantity was much increased on heating the soil. In both cases the heating increased the amount which could be obtained.

Adenine was found in small amounts in the Elkton soil, but was not obtained from the Sassafras. Heating effected no change in either case.

Guanine was found only in the Sassafras soil and is of especial interest, since this is the first time that it has been encountered in soil.

Cytosine, it is interesting to note, was found only in the heated samples of both soils. It was obtained in much larger amounts in the case of the heated Sassafras soil than in the case of the heated Elkton soil.

Histidine occurs in both soils, and a slight increase was noticed as the effects of heat.

Arginine, on the other hand, was found only in the heated Sassafras soil.

Creatinine was present in all cases.

Nucleoprotein Degradation Products.

If the principles discussed in an earlier section of this paper in regard to the breaking down of nucleoproteins, and of nucleic acids be applied to the interpretation of the results obtained by heating the Elkton and Sassafras soils, it becomes evident at once that hydrolysis of the nucleic acids of these soils has taken place. This is evidenced by the fact that in each case there was a diminution in the amount of nucleic acid obtained from the soils, and by the increase both in quantity and in number of the nucleic acid bases.

In the Elkton soil unheated, adenine and xanthine were found; on heating, the amount of xanthine increased, adenine was found as before, and in addition hypoxanthine appeared. The hypoxanthine had been formed by a nucleoside containing this base. The fact that it did not appear in the unheated soil may be due to an arrested decomposition of its antecedents, or to the fact that it has changed into xanthine or lower nitrogenous compounds. Similarly, the appearance of cytosine in the heated soil is undoubtedly due to the same cause, the action of heat on antecedents containing it.

In the Sassafras soil the changes are even more definite. In the unheated soil the only base found was hypoxanthine, but after heating there appeared guanine, xanthine, and cytosine, as well as a larger amount of hypoxanthine. The absence of guanine and xanthine in the unheated soil

TABLE II.—Organic Nitrogenous Compounds Isolated from Unheated and Heated Soils.
Elkton Silt Loam.

Unheated.	Heated.
Nucleic acid.	Nucleic acid.
Xanthine.	Xanthine.
—	Hypoxanthine.
Adenine.	Adenine.
—	—
—	Cytosine.
Histidine.	Histidine.
—	—
Creatinine.	Creatinine.

Sassafras Silt Loam.

Unheated.	Heated.
Nucleic acid.	Nucleic acid.
—	Xanthine.
Hypoxanthine.	Hypoxanthine.
—	—
—	Guanine.
—	Cytosine.
Histidine.	Histidine.
—	Arginine.
Creatinine.	Creatinine.

would seem to indicate that their antecedents were not subject to further decomposition under the existing soil conditions, or else they were rapidly changed into uric acid, urea, ammonia, &c.

These two soils, as already mentioned, have had the same general field treatment and have received the same kind of organic matter in the form of manures and crop debris, so that the nucleoproteins, nucleic acids, &c., which have entered into these soils, have been practically the same. The different results in the heated as well as in the unheated soils can only show that the decompositions occurring normally under the two different soil environments are biochemically different.

One difference between the two soils is found in the fact that the Elkton soil contains no antecedent compound which will yield guanine by heating. This fact may be explained by the assumption that the guanine antecedent, possibly guanosin, is changed to a xanthine antecedent in the soil. Colour is lent to this assumption by the fact that xanthine is found in both the unheated and heated Elkton soil, while guanine, as well as xanthine, is found in the heated Sassafras soil.

Another difference is in the adenine. This is found in Elkton soil and not in Sassafras soil, and any antecedent bodies seem to be absent from the latter soil. Hypoxanthine, on the other hand, into which adenine or its antecedents may change, is absent from the Elkton soil but present in the Sassafras.

Cytosine antecedents are present in both soils. The fact that cytosine is not found in the unheated soils may again be due to the permanency of the antecedent under both soil conditions, or else to the presence of factors, either chemical or biochemical, which have transformed it into uracil. Whether uracil exists in these soils, or, in fact, any other soil, cannot be experimentally determined at present owing to lack of characteristic derivatives or properties of uracil, although it seems probable that it must exist at least under certain conditions.

Protein Decomposition Products.

Two of the final products of protein hydrolysis appear in the present investigation. These are arginine and histidine. The latter was found in both soils, unheated and heated, but was found in greater amounts in the heated soil. Arginine was found only in the heated Sassafras soil. There is present, therefore, in the Sassafras soil a protein complex which acts as the antecedent of arginine. The question then remains, why is arginine absent from the unheated soil, and also, why is this antecedent body absent from the Elkton soil? Arginine, although a very common dissociation product of proteins, has nevertheless been found in only two other soils. This is rather peculiar in view of the fact that its close associate, histidine, has been found very often, a fact which is best explained on the supposition that arginine is very susceptible to change through biochemical influences. For instance, Kiesel (1909) found that the arginine in the juice of the green sprouts of lupine disappeared in the course of a four weeks' autolysis. In regard to the second part of the question as to the absence of any direct antecedent body no very

definite statement can be made, but it seems reasonable, since there is protein material in the soil, that the change of this material has not proceeded to such a stage that arginine could be produced by such a procedure as the one here employed. In other words, the biological factors in the Sassafras soil were such as to furnish an intermediary product which was dissociable by heat, and more readily decomposable in the soil. From this it would again appear that the biochemical factors are somewhat dissimilar under field conditions.

Concerning creatinine, nothing is known as to its immediate antecedent compounds, and no special lesson can be learned from the occurrence of this constituent in these soils.

To be continued).

A MILLION BOYS IN INDUSTRY SUPPORTING THE BURDEN OF WAR.

DR. ADDISON, M.P., the Minister of Munitions, states that the number of boys between the ages of fourteen and eighteen engaged in various occupations in this country is approximately 1,250,000, and that "their young shoulders are gallantly helping to support the burden of war." But while the war has heightened the value of the boy in the labour market it has intensified the problem of his welfare, and the Ministry of Munitions has issued a pamphlet on the subject which Dr. Addison commends to the attention of parents, employers, social workers, and teachers, in the hope that the problem may be brought nearer solution.

"The Boy in Industry" (H.M. Stationery Office, Kingsway, London, W.C. 2; 3d. net) puts the case of the factory lad clearly and without concealment of unpleasant facts. The ordinary boy of fourteen to eighteen years, states the author, is "unstable, wilful, elusive; the age is a critical one in his career, and he is receptive to influences both good and bad—chiefly bad." To-day various contributory causes make his position more precarious; the father's control is absent, and high wages are paid for his labour. "The boy knows nothing of the part he is to play either in the world or in his work," and finding himself regarded as a man he thinks that the sooner he apes man's follies the better.

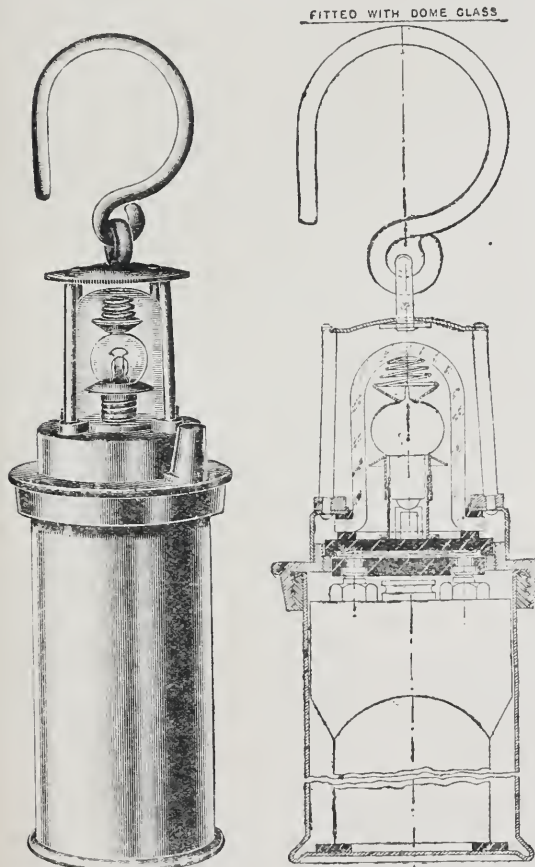
Various methods have been devised to stay this national waste, but the social and recreative agencies at work are insufficient. "A more highly developed system of engagement and control" from inside the industrial system is essential. This could be accomplished, the author insists, by the appointment in the factories of a sympathetic supervisor who would watch the personal interests of the boys. This officer would engage all the lads, would keep in touch with them at work and at play, and would encourage them in a wholesome outlook on life. Those concerned with the position of boys in industry would do well to read this "live" booklet from cover to cover, and to obtain the scheme for boy supervision in the munition factories from the Welfare Department, Ministry of Munitions, 6, Whitehall Gardens, London, S.W. 1.

THE "KINGSWAY" MINERS' ELECTRIC
HAND LAMP.*

THE chief points considered in developing this lamp have been efficiency of illumination over the full run of nine or ten hours, together with strong construction, durability of parts, and freedom from corrosion.

The *Accumulator* is of the absolutely non-spillable type. Many of the so-called non-spillable devices are only so over a limited period. If the lamps lie on their side for any length of time, acid leaks out of the gas vent holes, but with the accumulator used in this lamp, the lamp can be put in any position for any length of time without the least chance of acid escaping.

The *Accumulator Terminals* and switch arrangements have been specially designed to minimise corrosion,



THE LAMP COMPLETE.

GENERAL CONSTRUCTION
OF LAMP.

and particularly to stop corrosion during charging, at which time there is more liability of acid getting on to the terminals.

There are no springs of any kind attached to the accumulator, the necessary spring conductors being fastened in the lamp itself. As a consequence, it has been possible to make the terminals of the accumulator out of solid pieces of non-corroding material.

The spring controlled *Switch Contacts* are also of robust construction, consisting of strong flat springs with the upper ends screwed to the lampholder, and the lower ends

having the switch knobs rivetted into them. The construction is such that there is no possibility of "shorts" occurring by the displacement of the springs. The switch knobs also carry a pressure plate which maintains the pressure on the accumulator when the head is turned to the "off" position. No celluloid is used in the switchgear.

Reflectors.—The lampholder is provided with adjustable conical reflector to come below the lamp, and another conical reflector is supported on top of the lamp bulb. These reflectors are of polished nickel, and are so shaped that they considerably increase the illumination in the horizontal direction. In addition, an *External Reflector*, Patent No. 22227/14, can be fitted at a small extra charge; this consists of a curved nickelled reflector, which when not in use snaps on to the lamp case, and when in use partly surrounds the globe, concentrating the light over an angle of about 90°. The use of this external reflector has also the advantage, when lamps are being carried to the working face, of shielding anybody walking behind from the glare of the lamp.

Case.—The leaded steel case is fitted with a strong threaded sleeve which screws into the head of the lamp. The head is built on a strong brass casting, and is provided with a magnetic lock of simplest construction. No parts of this lock are accessible when the head of the lamp is screwed on, but when it is off the taking out of one screw allows the bolt and controlling spring to be removed and examined; the total number of parts for the lock being—the bolt, the spring, and the aforementioned screw.

AN ALL-RED TRADE ASSOCIATION.

New Industrial Grouping.

ALL students of Germany's economic progress are deeply impressed with the efficiency of her methods of collective industrial effort. Trade was developed by great trusts or by smaller companies working in conference, often under the general direction of bankers.

It has been repeatedly claimed that the Germans had reached a condition of "group consciousness" with which British individual consciousness contrasted unfavourably in industrial and other spheres.

Already before the war, however, there were in the United Kingdom very numerous trade associations which did a great deal to protect British industry during a period of dangerous political neglect.

The effect of war's revelations has been simply to show that such associations and combinations are of national advantage, and should be further encouraged and perfected for action on the return of peace.

Competitors and Co-operators.

Just as every producer is a consumer, and every consumer is, or ought to be, a producer, so can every competitor be a co-operator. It has been repeatedly demonstrated that as between the extremes, at one end cast-iron monopoly, and at the other end cut-throat competition, the middle way of collective effort by firms engaged in the same business, wisely controlled, gives the best results not only to Capital and Labour, but also to the market. The efficiency of production is increased, the standard of quality is raised, the wasteful cost of excessively competitive salesmanship is eliminated.

Many British firms have in the past been so keenly fighting each other that they could not at the same time fight the Germans. In the future they must do that first.

How Trade Meets Trade.

It is not only competitors who have interests in common. In the interaction of productive industry A trade obtains its raw materials from B trade, and its machinery from C trade, while it sells the goods so manufactured to D trade.

Each group has something to discuss with the other, and has much to gain by collective communication.

* Approved by the Home Office in the Safety Lamp Orders of November 16, 1916, Patent No. 102001/6. Manufactured by the General Electric Co., Ltd., Birmingham, London, and Manchester.

To provide for such communication between the industries of the Empire is the main purpose of the British Empire Producers' Organisation. Its creed is that British materials should be preferably diverted to British manufacturers and consumers, and should preferably be carried in British shipping; and, again, that the goods and machinery manufactured and produced should be preferably purchased throughout the Empire.

A certain amount of political reform is necessary to this end; but the B.E.P.O. recognises that beyond that it is for the organised industries to do the rest, and the progressive prosperity of the whole Empire depends largely on the vigour and direction of their collective efforts.

An Association of Associations.

As a clearing house or central exchange, the British Empire Producers' Organisation will provide and maintain the means of communication and co-ordination.

It does not admit the individual firm or company. It is an association of industrial associations and nothing else. Its control lies in the votes cast by trade associations as members.

The interests of the firm or company are left to the sectional trade association concerned.

The fiscal adjustments required by any trade are proposed by that trade. The only stipulation of the B.E.P.O. is that the principle of graduated preference for Empire Dominions and Allies must be observed if duties are to be imposed.

In every Dominion and Colony there are signs of increased alertness and firmer determination on the part of industrial associations, and the B.E.P.O. has already many powerful links in the chain of Imperial economic communication. Every new member association enters a community of interest representing numerous departments of vitally important industry, and contributes to the efficiency of a system planned to improve the welfare of all.—*Issued by the British Empire Producers' Organisation, Kingsway House, London, W.C. 2.*

BRITISH EMPIRE PRODUCERS' ORGANISATION.*

In the third year of the war the assembly of an Imperial Conference in London affords a fitting occasion for presenting a collective Address in the name of organised sections of productive industry, to welcome the representatives of the Dominions Overseas, and to express the confident hope that their visit will mark the beginning of a new era of social and economic development.

Coming from great territories remote from the European scene of conflict, their presence is doubly welcome to the people of the United Kingdom for the splendid spirit in which their citizens rose in defence of the Empire, and for the imperishable glory which their soldiers have won on so many battlefields.

We believe that in the vigour and discernment of their statesmanship, directed to the military and economic problems of the near future, means will be found for further strengthening the foundations of the free Britannic Commonwealth, and for reorganising its economic power and prosperity. The result of their labours is hopefully awaited by associations concerned with the efficient conduct of industrial organisation, in whose opinion the economic policy of this country and of the Empire should always in future be discussed with full regard to the interests and the responsibilities of our common Imperial citizenship.

We associate ourselves with the following principles which we believe now represent ideals appealing to the vast majority of the people of the Empire.

1. That the deepened sense of our unity of interest in the face of national danger, as between various classes of

the community, and as between the Dominions and territories of the Empire, must be recognised and maintained in all measures to be considered from the point of view of economic security and progress.

2. That the first claim on Imperial statesmanship is that remunerative employment shall be made available for all under conditions that will crown with comfort and prosperity the freedom for which we are now working and fighting.

3. That to this end the three great agencies of production, capital, labour, and science, should be systematically directed towards the development of the boundless resources of the Empire so that it may become more productive, not only of the prime necessities of life, but also of the essential materials of industry and of all departments of manufacture.

4. That the resolutions of the Paris Economic Conference provide a sound basis for national self development, and for maintaining mutually advantageous and privileged commercial intercourse between the Allied Powers.

5. That after the institution of such a system of reciprocal preferential arrangements as will give practical effect to the resolutions of the Paris Conference, which can best be settled in detail by conference with representative organised associations of manufacturers and producers, our next Imperial duty is to stimulate the employment of available resources of mechanical and chemical science for enhancing productive capacity, and so enriching the whole community.

6. That the system of general and technical education should be thoroughly revised to afford to all classes equality of opportunity for talent and industry.

7. That the State should, while facilitating general conditions, recognise and regularise the position of industrial organisations and give them additional responsibility for the efficient conduct of each section of industry. In conference with each other, with labour, and with the Government, they may thus found a system of industrial security and progress in true accord with the spirit of British enterprise as being capable of continuous adjustment to varying circumstances, and giving opportunity for the exercise of individual energy and original endeavour.

It is in the light of these principles that we believe an Imperial Economic System can be constructed worthy of our vast natural resources and of a manufacturing capacity greatly enhanced in volume and variety as the result of war demands. Further, we believe that a consistent policy aiming at the efficient and bounteous production of the wealth of the Empire by and for our own people will not only establish all British States on a higher plane of progress and prosperity, but will confer material and social advantages on the rest of the world.

List of Signatures to Memorial.

Agricultural Association of St. Vincent.
Agricultural Association of St. Lucia.
Agricultural Commercial Society of St. Lucia.
Antigua Agricultural and Commercial Society.
Associated Chambers of Manufacturers in Australia.
Association of Master Painters in Scotland.
Associated Public Calenders, Sack Sewers, and Packers (Dundee).
Associated Public Dyers (Dundee).
Australasian Chamber of Commerce in London.
Ayrshire Founders' Association.
All-for-Empire League (Wellington, N.Z.).
Association of Tar Distillers.
Barbadoes Agricultural Society.
Barbadoes Chamber of Commerce.
Belfast Master Bootmakers' Association.
Bristol Channel and West of England Corn Trade Association.
British Acetylene and Welding Association.
British Agricultural Section (B.E.P.O.).
British Association of Trade and Technical Journals.

* Memorial presented to the Members of the Imperial War Council on behalf of Organised Industries of the Empire.

British Cotton and Wool Dyers' Association.
British Elastic Webb Manufacturers' Association.
British Electrical and Allied Manufacturers' Association.
British Empire Sugar Machinery Manufacturers' Association.
British Empire Producers' Organisation.
British Engineers' Association.
British Photographic Manufacturers' Association.
British Rubber Tyre Manufacturers' Association.
British Sugar Beet Growers' Society.
Behar Planters' Association.
Cable Makers' Association.
Canadian West Indian League.
Ceylon Association in London.
Ceylon Planters' Association.
Cycle and Motor Cycle Manufacturers' and Traders' Union.
Dundee and District Spinners' and Manufacturers' Association.
Electrical Contractors' Association.
Fertiliser Manufacturers' Association.
Hinckley and District Hosiery Manufacturers' Association.
Incorporated Association of British Toy Manufacturers and Wholesalers (Manchester).
Incorporated Federated Association of Boot and Shoe Manufacturers of Great Britain and Ireland.
Indian Sugar Producers' Association.
Indigo Planters' Association.
Institute of British Carriage Manufacturers.
Iron Masters' Association (New Zealand).
London Colour, Paint, and Varnish Manufacturers' Association.
London Copra Association.
London Jute Association.
London Master Stevedores' Association.
Mauritius Chamber of Agriculture.
Mauritius Chamber of Brokers.
Mauritius Chamber of Commerce.
Mincing Lane Sugar Trade Association.
Natal Sugar Association.
National Association of Master Plumbers.
North Charterland Exploration Co. (1917), Ltd.
Nottingham Lace Manufacturers' Association.
New Zealand Farmers' Union.
New Zealand Ironmasters' Association.
Ossett Chamber of Commerce.
Pianoforte Manufacturers' Association.
Redditch and District Needle and Fishing Tackle Employers' Association.
River Thames Dry Dock Proprietors and Ship Repairers' Association.
Rubber Growers' Association.
Royal Agricultural and Commercial Society of British Guiana.
Scottish Association of Master Heating, Ventilating, and Domestic Engineers.
Scottish Employers' Federation of Iron and Steel Founders.
Scottish Master Bevelers and Silverers' Association.
Scottish Master Plasterers' Association.
South African Federated Chamber of Industries.
Southampton Engineering and Shipbuilding Employers' Association.
South Wales and West of England Federation of Master Bakers and Millers' Association.
Sugar Association of Lancashire.
Suva Chamber of Commerce (Fiji).
Trinidad Chamber of Commerce.
Trowbridge Chamber of Commerce.
Tobago Planters' Association.
United Planters' Association of Southern India.
West India Committee.
West India Association of Glasgow.
West India Association of Liverpool.
West of Scotland Iron and Steel Founders' Association.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, April 26, 1917.

Sir J. J. THOMSON, O.M., President, in the Chair.

PAPERS were read as follows:—

"The Effective Inertia of Electrified Systems Moving with High Speed." By G. W. WALKER, F.R.S.

If it is assumed that an electron moving with speed C (where C is velocity of light) becomes deformed so that surface is of the form $(1-k^2) - x^2 + y^2 + z^2 = a^2$, Lorentz has shown by the "quasi-stationary" assumption, that the inertia for longitudinal inertia is $m_0(1-k^2)^{-\frac{1}{2}}$, and for transverse inertia $m_0(1-k^2)^{-\frac{3}{2}}$. The same results follow from Einstein's "relativity" theory.

In the paper the inertia is determined by a method developed in a former paper (*Phil. Trans.*, A, ccx., 145), which depends directly on the primary equations, and is free from the error that the quasi-stationary method may introduce.

The results are that, for a "contracted" electron the longitudinal inertia is—

$$m_0(1 - \frac{1}{5}k^2)(1 - k^2)^{-\frac{3}{2}},$$

and the transverse inertia is—

$$m_0(1 + \frac{11}{60}k^2)(1 - k^2)^{-\frac{1}{2}}.$$

"Composition of X-Rays from various Metals." By G. W. C. KAYE, D.Sc.

The X-rays from a bulb excited by low voltages (10,000 to 50,000 volts) are rich in the characteristic radiation of the anticathode.

In the case of iron, nickel, and copper the amount of K-radiation lies between 80 and 90 per cent.

In the case of platinum the proportion of L-radiation is from 40 to 60 per cent.

Evidence of characteristic radiations softer than the K and L radiations has been obtained.

"Germicidal Action of Ultra violet Radiation and its Correlation with Selective Absorption." By C. H. BROWNING, M.D., and S. RUSS, D.Sc.

1. A new method is described which renders it possible to determine what portion of the ultra-violet spectrum is most effective in germicidal action and, further, to specify the wave-length of the radiation at which such action practically ceases.

The method consists in exposing a thin film of organisms spread on a nutrient surface, such as gelatin or agar, to the spectrum from a tungsten arc. The image of the slit of the quartz spectrometer used produces a permanent effect upon the bacterial film over a certain range of wave-lengths. This germicidal action becomes apparent on incubation at 37° C. subsequent to the exposure; thus a copious growth occurs except in those regions where the organisms have been killed. Records of such action are obtained which resemble a photograph of the spectral lines.

2. The method has been applied to test the range of susceptibility of a number of different pathogenic organisms. By the process described it is possible to expose cultures of two different organisms simultaneously to the same intensity and character of radiation. The ranges of susceptibility of *B. typhosus* and *B. coli* are closely similar, and practically the same as those of organisms such as *staphylococcus pyogenes aureus* and the *meningococcus*.

3. A striking feature of the germicidal action of the radiation in question is its abrupt termination at a wave-length of about 2960 A.U.

4. It has been possible to correlate this feature with "selective absorption," for it is found that the organisms exhibit marked absorptive power for just those rays which have germicidal action.

"Morphological Studies in the Life-histories of Bacteria."
By E. C. HORT.

According to current theory the life-history of the "lower" bacteria is one of great simplicity, reproduction taking place—apart from endosporulation, in certain cases, of a special type—solely by transverse binary fission.

This theory is mainly based on the unquestioned fact that transverse binary fission is the rule in standardised laboratory cultures. Aberrant morphological types have from time to time been recorded in the past, but these have been usually dismissed either as contaminants, as involution forms, or as examples of mutation.

In the present communication evidence is produced to show that the life-cycle of the "lower" bacteria, as illustrated by the members of the enteric group, so far from being solely represented by perpetual binary fission, is one of great complexity, and includes an invisible, or almost invisible, stage. The nature of the evidence presented excludes the presence of contaminants, or of "involution" forms, as reasonable explanations of the recorded observations, and throws grave doubt on the adequacy of the mutation theory to explain morphological aberrancy from type—laboratory type—amongst the bacteria.

The evidence, in short, suggests that the true significance of these "aberrant types" has hitherto escaped us precisely because we have—for purposes of ready identification—standardised laboratory media for the cultivation of bacteria, and have not always remembered that their natural habitat, both as saprophytes and as agents of disease, is in a perpetual state of biochemical flux.

The evidence consists of a series of camera lucida drawings and microphotographs of fresh films of killed organisms of the enteric group, together with drawings of living organisms watched, during the process of development, on the warm stage.

CHEMICAL SOCIETY.

Ordinary Meeting, April 19, 1917.

Prof. W. J. POPE, M.A., D.Sc., F.R.S., President,
in the Chair.

THE PRESIDENT referred to the deaths of the following Fellows:—Maurice Kemp-Welch (killed in action), Taylor Cook, John Kerr Forrest, Thomas Utrick Walton.

The following announcements were made:—

1. That the following Committees had been appointed for the year 1917-18:—

Finance Committee—Messrs. E. G. Hooper, G. T. Moody, Sir E. Thorpe, Sir William A. Tilden, and the Officers.

House Committee—Messrs. Horace T. Brown, R. Messel, J. E. Reynolds, Alexander Scott, J. M. Thomson, Sir William A. Tilden, and the Officers.

Library Committee—Messrs. B. Dyer, W. Gowland, A. Harden, J. T. Hewitt, C. A. Keane, A. R. Ling, T. M. Lowry, J. M. Thomson (Chairman), Sir William A. Tilden, J. A. Voelcker, the Editor, and the Officers.

Publication Committee—Messrs. A. Chaston Chapman, A. Harden, T. A. Henry, T. M. Lowry, F. L. Pyman, Alexander Scott, G. Senter, J. F. Thorpe, and the Officers.

Research Fund Committee—E. C. C. Baly, Horace T. Brown, F. G. Donnan, H. J. H. Fenton, P. F. Frankland, A. Lapworth, W. H. Perkin, Alexander Scott, J. F. Thorpe, W. P. Wynne, and the Officers.

2. That owing to ill-health, Dr. Horace T. Brown is unable to deliver his lecture entitled "The Principles of Diffusion—their Analogies and Applications," on May 17, as previously announced. The Council has postponed for

a time the delivery of this lecture, and the usual Ordinary Scientific Meeting will be held on that date.

Certificates were read for the first time in favour of Sir Charles Henry Bedford, D.Sc., M.D., LL.D., 166, Piccadilly, W.; Manmatha Nath Das, B.A., 19, Waverley House, Kenton Street, W.C.; David Richard Davey, 38, Harvey Road, Hornsey, N.; James Nelson Edmund Day, A.R.C.S., 24, Marlborough Road, St. Albans; James Garfield Detwiles, B.Sc., Port Arthur, Texas, U.S.A.; Albert Henry Frankland, Craig-y-don, Marshall Avenue, Crossgates, near Leeds; Harry Gailop, B.Sc., Craigdale, Forbes Road, Faversham, Kent; Kenneth Claude Devereuse Hickman, A.R.C.S., 11, Carlyle Square, Chelsea, S.W.; Cuthbert Baring Horwood, B.Sc., Tunstall, Suffolk; George Inglis Hudson, 31, Bay Street, Glebe, Sydney, Australia; William King, Empangeni Rail, Zululand, South Africa; Frederick George William Knapman, B.Sc., 28, May Street, W. 14; Robert Iltyd Lewis, B.Sc., 8, Newton Road, Faversham, Kent; Joseph Patrick Madden, Springfield, 30, The Avenue, Hitchin; Joseph Harold Mandelberg, M.A., Redclyffe, Victoria Park, Manchester; John Montgomery, 66/68, Donegall Street, Belfast; James Patrick O'Callaghan, 36, Tyrwhitt Road, Brockley, S.E.; Cedric Gerard Verver, A.R.C.S., 11, Carlyle Square, Chelsea, S.W.; Howell Williams, 14, Camberwell Terrace, Antrim Road, Belfast.

The following papers were read:—

"Studies in Catalysis. Part VI. The Mutual Influence of Two Reactions proceeding in the same Medium." By R. O. GRIFFITH, A. LAMBLE, and W. C. MCC. LEWIS.

"Studies in Catalysis. Part VII. Heat of Reaction, Equilibrium Constant, and Allied Quantities from the point of view of the Radiation Hypothesis." By W. C. MCC. LEWIS.

"The Alkaloids of Ipecacuanha." (Part II.). By F. L. PYMAN.

SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS.

Ordinary Meeting, May 2, 1917.

Mr. GEORGE EMBREY, President, in the Chair.

A CERTIFICATE was read for the second time in favour of Capt. N. M. Comber, A.R.C.S., B.Sc. (Lond.).

Certificates were read for the first time in favour of Charles V. Bacon, 1, Day Street, New York City, Analytical and Consulting Chemist, proposed for nomination by the Council; Kapilram Hardevram Vakil, B.A. (Bombay), B.Sc. Tech. (Manch.), of Bombay.

The following papers were read:—

"Rapid Method for the Determination of Nickel and Cobalt in Ores and Alloys." By W. R. SCHOELLER, Ph.D., and A. R. POWELL.

The method is based on the insolubility of hexammine-nickelous and hexamminecobaltous iodide in a solution containing 4 per cent of potassium iodide and 80 per cent by volume of strong ammonia. Ferric iron and other trivalent metals are not precipitated in presence of sufficient tartaric acid. Zinc, magnesium, and arsenic do not interfere. Lime, if present in large amount, should be previously removed as sulphate in 50 per cent alcohol. In the absence of manganese, cadmium, and copper, the assay is carried out as follows:—

The sample is dissolved in nitric acid, the excess of acid is boiled off, and sufficient tartaric acid added to prevent precipitation of iron, &c. The cold solution, which should have a bulk of less than 15 cc., is then treated with four times its volume of strong ammonia, followed by the necessary excess of potassium iodide in cold saturated solution. The precipitate is filtered off, washed with ammoniacal 4 per cent iodide solution, re-dissolved in dilute hydrochloric acid and a little sulphur dioxide, and

the insoluble gangue filtered off. In the filtrate the cobalt is precipitated as cobalt ammonium phosphate, which may be titrated with $N/5$ acid; the nickel filtrate is treated with cyanide. Manganese, copper, and cadmium, if present, are also precipitated as complex iodides. Copper may be eliminated as cuprous iodide by adding sulphur dioxide to the acid solution of the precipitate. Cadmium very rarely occurs in nickel and cobalt ores; manganese is the one seriously interfering element, and must be separated by a hydrogen sulphide treatment in acetic acid solution.

An assay by this method can be completed in two to four hours. The authors hope to deal with the assay of manganiferous ores, cobalt-steel, &c., in a subsequent paper.

"Note on Opium Poisoning Cases." By JOHN WEBSTER, F.I.C.

Two cases of morphine poisoning are described; one in which one dose only was taken, and the other that of a confirmed drug taker. In the first case strong reactions from the viscera were obtained and morphine in fair quantity, whereas in the second the reactions were slight or even doubtful.

"Determination of Unsaponifiable Matter in Oils, Fats, and Waxes." By JOHN M. WILKIE, B.Sc., F.I.C.

This determination is often troublesome owing to emulsification. By adopting a definite concentration of alcohol and ether before extraction, best obtained by the use of $2/N$ alcohol KOH for hydrolysis, the formation of emulsions may be entirely prevented and the determination finished in thirty minutes after saponification.

The trouble experienced in the analysis of bees' and other waxes, lanoline, &c., may be entirely eliminated by using 0.5 gm. of wax and 4.5 gm. of castor oil, extracting as usual, and making a correction for the unsaponifiable matter in the castor oil.

SOCIETY OF GLASS TECHNOLOGY.

Ordinary Meeting, April 18, 1917.

Mr. FRANK WOOD, B.Sc., in the Chair.

A DISCUSSION on "Machinery and Labour Saving Devices in the Glass Factory" was opened by Mr. A. M. ROWLAND, Chief Technical Assistant, Machine Tool Department, Ministry of Munitions.

In his preliminary remarks, Mr. Rowland emphasised the need for well-planned works, because most glass factories—owing to the fact that they had been built on the patchwork system—were badly laid out. Spaciousness was very necessary both from the point of view of overlooking of workmen and for visibility. Everything should be available and not hidden; visibility being a point conducive to good workmanship. A works, too, should be accessible, both for its workpeople and for the reception and dispatch of materials. Great attention should be paid to lighting, and arrangements should be made for gradation of light, if necessary. One often found, for example, that a storeroom (where visibility is so essential) was quite dark. For glass cutting and polishing a room with a northern aspect was to be advocated. In every works a study should be made of the best means of transport, particularly in regard to the reception of raw materials, the transport of materials inside the works, and the delivery of the finished articles. Overhead runways and not rails were to be advocated for a glasshouse, with a series of standardised trucks, whilst the raw material should be transported to the store by means of a bucket conveyer. Conveying bands, too, could be employed inside the shops for the transport of glass articles to the Lehr, and when cold to the sorting room. Motor lorries should be used for delivery of finished goods, as they avoid many handlings of cases—a point of great importance in the glass trade. If glass manufacturers could

evolve a lorry of the particular type needed, the motor-car manufacturer would do the rest.

Returning to the works, much labour can be saved by proper batch handling. Grading, mixing, grinding, and weighing all require proper arrangement, so that as little manual labour as possible is necessary. Expense, and labour too, can be saved in the utilisation of waste heat.

Commenting next upon particular glass processes, the speaker drew attention to the forward strides that were being taken in the use of compressed air in glass blowing. The introduction of the Owens machine was a triumph for automaticity. In Germany the automatic machine was worshipped; in England it was hated, yet it conferred many advantages. The manufacture of glass tubing could certainly be improved if some automatic or semi-automatic method were used.

Much labour could be saved the glass manufacturer by an interchange of tools and moulds, whilst some means should be sought whereby the taper of all stoppers should be the same, so that a stopper of a particular type would fit any bottle of that particular type. In conclusion, the speaker pointed out that much information regarding new and useful machinery was available at the Ministry of Munitions. Several problems had been worked out, and others were in the process of solution, and the information was at the disposal of glass manufacturers for the asking.

Mr. F. R. DIXON-NUTTALL continued the Discussion, confining his remarks chiefly to the labour-saving devices employed in America in connection with the Owens machine. He gave a most interesting and succinct account of the up-to-date methods used in grinding, mixing, and conveying batch to the furnace. The batch materials are stored in huge receptacles, connected to the furnace floor by hoppers. To obtain a mixed batch, ready for filling on at the furnace, a workman runs an electrically propelled truck beneath each hopper, which automatically discharges the requisite amount of material. Cullet which has been finely ground can also be added from a hopper. When the truck is full it runs off to the furnace; on its way thither the batch is thoroughly mixed by a revolving mechanism inside the truck.

Mr. S. N. JENKINSON exhibited a very interesting and instructive series of lantern slides showing various machines used in the glass trade, including machines for cutting off, re-melting, puntying, grinding, slicing, etching, shaping marbles for soda-water bottles, &c. Pictures of Lehrs, batch mixers, automatic boys, &c., were also shown.

A paper by Mr. G. E. ALEXANDER, in the unavoidable absence of the author, was communicated by Dr. TURNER.

The paper dealt with the Owens machine, and showed how it had revolutionised the bottle industry in the United States owing to rapidity of production and reduced prices. Bottles ranging in capacity from one-tenth ounce to 13 gallons could be made on this machine, in shape and finish as good as the hand-made products. Syphons, tumblers, lamp-glasses, electric bulbs, carboys, &c., were all being turned out successfully. As many as 75,000 quart bottles could be produced by one machine in a twenty-four hour day. Specimens of various bottles made on an Owens machine were exhibited. No human aid was needed until the bottle was delivered cold at the mouth of Lehr—two types of which were in use, one for small and one for large bottles. Both had proved a success.

A description of the batch mixing and supply arrangements in force in an American factory, following on the lines of Mr. Nuttall's paper, was also included, it being pointed out that one man could keep six to eight furnaces supplied with batch on an eight-hour shift.

A long and animated discussion followed the remarks of the principal speakers, the following gentlemen taking part:—Prof. W. F. G. Fearnside, Dr. P. G. H. Boswell, Messrs. Durants, Simpson, Sweeting, Munro, Steel, and Swann.

CORRESPONDENCE.

DIGESTIBILITY OF 80 PER CENT FLOUR.

To the Editor of the Chemical News.

SIR,—Will you kindly allow me to make a clerical correction in the above mentioned comment, which appeared in the CHEMICAL NEWS (cxv., 200).

In paragraph 6 it is stated that in a digestibility experiment described in U.S.A. Bulletin 156, Subject 3, digested from coarsely-ground wholemeal only 40.5 per cent of the protein. This figure ought to be 75.6. When the bran was ground to a uniform fineness 90.0 per cent of the protein was assimilated, only 0.6 per cent less than was digested from 70 per cent white flour.

In the following paragraph relating to a paper supplied to the Royal Society by the late Sir Lauder Brunton, F.R.S., on the digestion of wholemeal, the reference should be to *Proceedings*, 45, 1888, instead of to *Transactions*, No. 45.

There is an interesting report about digestibility experiments on the food value of different kinds of bread undertaken for a month by the Societa Umanitaria di Milan, in *La Revue Generale des Sciences*, November, 1915. It is gratifying to learn that although adverse to the use of ordinary brown bread, which has never been advised by the Bread and Food Reform League, the report states that the 80 per cent bread now used in Italy, and advocated by the League for many years, is "an excellent bread, the use of which should be encouraged in normal times."

Thanking you most gratefully for the prominent attention you have directed to this subject, I am, &c.,

MAY YATES,

Hon. Sec. Bread and Food Reform League.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Bulletin de la Société Chimique de France.

Vol. xxi.-xxii., No. 3, 1917.

Catalytic Hydrogenation by Formic Acid, and Products of Catalytic Condensation of Ordinary Acetone.—Alph. Maihe and P. de Godon.—Under the influence of divided metals formic acid may be decomposed according to either of the two following equations:— $\text{HCO}_2\text{H} = \text{CO}_2 + \text{H}_2$ or $\text{HCO}_2\text{H} = \text{H}_2\text{O} + \text{CO}$. The metals can be divided into three groups, according to their action. (1) Those—like copper, nickel, stannous oxide, zinc oxide—which bring about equation I.; (2) those—like Ti_2O_3 , alumina, silica—which bring about equation II.; (3) a third group—comprising thoria, blue oxide of molybdenum, ferrous oxide, &c.—which bring about both reactions. When the hydrogenation of acetone by the nascent hydrogen evolved from formic acid in presence of copper or nickel is studied, it is found that the normal reaction indicated by Darzens always occurs, viz., the formation of the hydrocarbon of the phenyl-formic series. When acetone is hydrogenated in presence of nickel at temperatures between 300° and 350° it is transformed into oxide of mesityl and more condensed products, which are then totally or partially hydrogenated by the hydrogen in presence of the nickel.

In affectionate remembrance of ELLEN ("NELLIE") LADY CROOKES, my beloved Wife, who passed into Spirit Life on May 10th, 1916, after more than sixty years of sweet companionship.

"Birthless and deathless and changeless remaineth the Spirit for ever; Death hath not touched it at all, dead though the house of it seems."

MEETINGS FOR THE WEEK.

MONDAY, 14th.—Biochemical Society, 5.30. "Alleged Antineuritic Properties of α -Hydroxypyridine," by A. Harden and S. S. Zilva. "Colour Effects produced by Two Groups of Organisms upon Protein (Casein) and some Amino-acids," by E. C. V. Coruish and R. Stenhouse Williams. "Presence in Blood and Tissues of certain Growth Factors for the Gonococcus," by S. W. Cole and D. Jordan Lloyd. "Occurrence of the Fat-soluble Accessory Substance in certain Animal and Vegetable Fats," by J. C. Drummond.

TUESDAY, 15th.—Royal Institution, 3. "Architectural Design in Organisms—The Laws of Growth and Form," by Prof. D'Arcy W. Thompson, C.B.

WEDNESDAY, 16th.—Royal Society of Arts, 4.30. "The Blind Sufferers from the War, and Their Future Employment," by Sir C. Arthur Pearson, Bart.

Society of Glass Technology, 2.15. (At the Institute of Chemistry, 30, Russell Square, W.C.1.) "Some General Observations on Glass," by Prof. Herbert Jackson.

THURSDAY, 17th.—Royal Institution, 3. "The Chromosome Theory of Heredity and the Alternatives," by Prof. W. Bateson.

Royal Society of Arts, 4.30. "The Development of Banking and Thrift in India," by A. C. Chatterjee.

Royal Society. (The Bakerian Lecture). "The Configuration of Astronomical Masses and the Figure of the Earth," by J. H. Jeans.

FRIDAY, 18th.—Royal Institution, 5.30. "The Complexity of the Chemical Elements," by Prof. Frederick Soddy.

SATURDAY, 19th.—Royal Institution, 3. "The Electrical Properties of Gases," by Prof. Sir J. J. Thomson, O.M.

TO comply with Regulation 8(b) of the Defence of the Realm Act, advertisements from firms whose business consists wholly or mainly in Engineering, Shipbuilding, or the production of Munitions of War, or of substances required for the production thereof, must include the words "No person resident more than ten miles away or already engaged on Government work will be engaged."

Chemist (43) with Works and Biological experience, seeks Post, Research preferred.—Address, D. M., CHEMICAL NEWS Office, 16, Newcastle Street, Farringdon Street, London, E.C. 4.

CHEMICAL ENGINEER (Manager) wanted by Controlled Firm for Works in Lancashire. Permanency.—State age, salary, experience, and organising ability, to Box "B. 36," Lee and Nightingale, Liverpool.

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NOBEL'S EXPLOSIVES COMPANY, Ltd., ARDEER FACTORY, STEVENSTON.

There are at present several vacancies on the Staff of the above Factory for men suitable for training for the control of manufacture.

Applicants, who must be qualified Chemists, preferably possessing a University Degree or its equivalent, should submit full details of their training and experience to THE MANAGER, Research Section, Ardeer Factory, Stevenston.

THE CHEMICAL NEWS

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A STATISTICAL STUDY OF ORGANIC SERIES.

By W. R. FORBES, B.Sc. (Lond.).

IN the subjoined an attempt is made to compare organic series by finding their coefficient of variation. The statistical method employed is outlined in Watts's "Heredity." The boiling-points of the series of organic compounds are expressed in absolute temperature. The average is then obtained. Each datum is subtracted from the average (1) and the result squared (2). The sum of these squares is then divided by the sum of the data giving us the square of the standard deviation. The deviation expressed as a percentage of the average gives us the coefficient of variation. The series are selected so as to show in each case equal additions of (CH₂).

Series.	Boiling-point.	1.	2.
H.CO ₂ H	374	50	2500
CH ₃ CO ₂ H	391	33	1089
C ₂ H ₅ CO ₂ H	414	10	100
C ₃ H ₇ CO ₂ H	435	11	122
C ₄ H ₉ CO ₂ H	458	34	1156
C ₅ H ₁₁ CO ₂ H	473	49	2401

Average 424

Standard deviation = 1.6.

Coefficient of variation = 0.37.

CH ₃ OH	339	42	1764
C ₂ H ₅ OH	351	30	900
C ₃ H ₇ OH	370	11	122
C ₄ H ₉ OH	389	8	64
C ₅ H ₁₁ OH	410	29	841
C ₆ H ₁₃ OH	430	49	2401

Average 381

Standard deviation = 1.4.

Coefficient of variation = 0.36.

Benzene	353	54	2916
Toluene	383	24	576
Xylene	413	6	36
Cumene	442	35	1225
Cymene	448	41	1681

Average 407

Standard deviation = 1.7.

Coefficient of variation = 0.41.

CH ₄	109	133	17889
C ₂ H ₆	183	59	3481
C ₃ H ₈	255	7	49
C ₄ H ₁₀	274	32	1024
C ₅ H ₁₂	309	67	4489
C ₆ H ₁₄	342	100	10000

Average 242

Standard deviation $\sqrt{25.4} = 5.0$.

Coefficient of variation = 2.0.

Coefficient of Variation.

Series.	C.v.
Alcohol	0.36
Carboxylic acid	0.37
Benzene	0.41
Paraffin	2.0

In the paraffin group which contains no oxygen or hydroxyl group, it appears that the coefficient of variation lies right apart those of the other series considered. The coefficient for the benzene series comes remarkably near that for the alcohol and carboxylic acid series, which are almost identical. In considering the alcohol and carboxylic acid series we must remember that each contains an OH group. It therefore appears that the (H₂) of the alcohol series corresponds to the (O) of the carboxylic acid series in its influence on the boiling-point for equal additions of (CH₂).

The benzene series contain no oxygen or hydroxyl groups, but the difference of the coefficient of variation from that of the paraffin series can be accounted for by the structure of the benzene nucleus. The approximation to the coefficient of variation in the alcohol and carboxylic acid series points to an equivalence of the doubtful benzene bond to (O or H₂), and so would tend to support the double bond formula for the benzene nucleus rather than the centric formula.

Therefore this statistical study appears to furnish additional evidence as to the nature of the benzene ring and to the theory of the double bond.

Marlborough, New Zealand.

THE ORGANIC NITROGEN COMPOUNDS OF SOILS AND FERTILISERS.*

By ELBERT C. LATHROP, Ph.D.

(Concluded from p. 222).

The Decay of Proteins in the Soil.

THAT constant decomposition of proteins is going on in agricultural soils is clearly shown by the two preceding investigations. This is evidenced, first, by the fact that a number of primary protein decomposition products are regularly occurring soil constituents, and by the additional fact that side by side with these simpler nitrogenous compounds there are present in soils, complexes, themselves proteins or nucleoproteins, or very nearly akin to these. Such evidence shows the importance of a thorough knowledge of the biochemistry of the decay of protein materials in soils in finally elucidating the changes which take place normally in the organic nitrogenous matter of soils, and the nature of the compounds which result from these changes.

This subject is not only of theoretical importance, but is of practical value as well. Not only do proteins from the *débris* of plants growing in the soil accumulate there, but there are added to most agricultural soils stable manure, organic fertilisers, and green manuring crops. All of these manures contain considerable quantities of proteins or complexes closely related to the proteins. The question of the availability or agricultural value of these fertilisers is only to be answered either by directly determining the effects of the products of decay of these materials upon the plants growing in the soil, or by determining by chemical means certain facts concerning their nature. It is obvious that a knowledge of the normal decay of protein material in soils will materially aid in solving such a problem.

This investigation was undertaken for the purpose of studying the changes taking place in the protein material of a high-grade organic nitrogenous fertiliser when added to an agricultural soil. Since ammonia formation is but one step in this process it becomes of interest to know from what portion of the protein molecule this ammonia is formed; for how long the protein itself or the primary decomposition products of the protein can persist in the

* Contribution from the Laboratory of Soil Fertility Investigations communicated by Dr. Oswald Schreiner, and published by permission of the Secretary of Agriculture. From the *Journal of the Franklin Institute*, clxxxiii., No. 3.

soil, and finally to gain some insight into the nature of the compounds formed by the action of the micro-organisms in their life processes.

The Proteins Studied.

Dried blood, which was chosen for this investigation, is composed almost entirely of various animal proteins and the commercial product is of fairly constant composition. Abderhalden (1898) reports figures on the composition of the blood of cattle, sheep, pigs, horses, and goats, which show that a mixture of the blood of these animals should contain about 200 parts of solid matter per 1000 parts of blood. Of these solids about 54 per cent is hemoglobin, and about 32 per cent albumin, or approximately 86 per cent is composed of proteins, exclusive of any nucleoproteins or nucleic acids, which undoubtedly are also present.

The dried blood used in this investigation was purchased in the open market, and contained 13.92 per cent of total nitrogen. Two samples of dried blood were hydrolysed by boiling with hydrochloric acid, and the various forms of nitrogen in the hydrochloric acid extract were then estimated according to the nitrogen partition method proposed by Van Slyke. The results so obtained are presented in Table III. Cystine nitrogen was not determined, and the small amounts of cystine nitrogen in the blood would be included with nitrogen in the form of arginine, histidine, and lysine.

TABLE III.—The Forms of Nitrogen in Dried Blood and in the Experimental Soil. Results Expressed in Per Cent of Hydrolysable Nitrogen.

Form of nitrogen.	Dried blood.	Soil.
Amide	6.854	7.008
Melanin	2.60	4.767
Arginine	7.517	7.601
Histidine	12.523	12.366
Lysine	11.517	10.093
Monoamino	57.057	58.220
Non-amino	1.479	0.312
Total.. .. .	99.547	100.367

The Soil Used.

The soil chosen for use was a Norfolk fine sandy loam taken from a cantaloupe field near Raleigh, N.C. The soil was in a high state of cultivation, and had received both mineral fertilisers and stable manure. It was found to contain 0.0301 per cent of total nitrogen. The soil was passed through a 40-mesh sieve and dried in vacuum.

Forty pounds of soil were mixed with about 3 pounds of dried blood by sieving the two together until samples taken from different parts of the mixture gave duplicate analyses for total nitrogen. The total nitrogen in the soil thus prepared was found to be 0.8945 per cent. The ammonia in the prepared soil was found to be 0.0005 per cent.

The soil was made up to a 10 per cent moisture content, and was kept in a stoneware jar covered with perforated wrapping paper to exclude dust. The decomposition was allowed to proceed at the temperature of the laboratory.

During the first period of eighteen days the soil was maintained at a moisture content of 10 per cent, and was mixed several times by hand during that period to promote aeration. Later on, however, the soil was restored to the 10 per cent moisture content every five to eight days, and on two occasions it was allowed to dry out completely. At each addition of water to the soil it was turned out of the jar, and thoroughly mixed. The total length of the experiment was 240 days, during which time samples of the soil were taken at the following intervals:—

1.	18 days
2.	44 "
3.	86 "
4.	148 "
5.	240 "

Nitrogen Partition.

By the use of the methods outlined the nitrogen was separated into the following:—(1) Total nitrogen in the soil; (2) total nitrogen in hydrochloric acid solution; (3) ammonia nitrogen in the soil; (4) ammonia nitrogen in hydrochloric acid solution; (5) melanin nitrogen; (6) nitrogen precipitated by phosphotungstic acid, reported as arginine, histidine, and lysine nitrogen; (7) nitrogen in the filtrate from the phosphotungstic acid precipitate, reported as monoamino acid nitrogen and non-amino nitrogen.

By subtracting the amount of ammonia nitrogen found in the soil (3) from the amount of ammonia nitrogen found in the hydrochloric acid (4) the amount of nitrogen in the soil in the form of the amide group in proteins or as acid amides may be obtained. This is reported as amide nitrogen. The amount of nitrogen in the soil in the form of proteins or protein decomposition products, with the exception of ammonia nitrogen, may be obtained by subtracting the amount of ammonia nitrogen in the soil (3) from the amount of total nitrogen in hydrochloric acid solution (2). This is reported as "hydrolysable" nitrogen. The amount of nitrogen in all of the various fractions was determined by the Kjeldahl method, which does not include nitrate nitrogen unless large amounts of reducing substances are present; such may be the case, however, with some of the Kjeldahl analyses, and any nitrate nitrogen therefore included in a Kjeldahl determination would be reported as non-amino nitrogen.

In regard to the nitrogen reported in this investigation as amide nitrogen it might be stated that it is difficult to conceive in the present state of our knowledge of any other soil compounds than the various proteins which contain the amide group, or the acid amides themselves which would resist heating *in vacuo* with calcium hydroxide, and subsequently split off ammonia on heating with hydrochloric acid.

The melanins are at present undefined and no significance can be attached to the figures obtained.

The nitrogen reported as monoamino acid nitrogen includes all nitrogenous compounds not precipitated by calcium hydroxide or not volatile in its presence *in vacuo*, not precipitated by phosphotungstic acid in the concentrations used, and containing a free amino group which will react with nitrous acid to produce free nitrogen.

The greatest inaccuracies occur in the diamino acid fraction, and these are distributed between arginine, histidine, and lysine nitrogen. This group includes all nitrogenous compounds which are precipitated by phosphotungstic acid, excepting ammonia and melanin nitrogen.

The nitrogen reported as non-amino nitrogen includes all nitrogenous compounds not accounted for in the above, and may include small amounts of nitrogen present in the soil in the form of nitrates.

The results obtained by the methods outlined are presented in Tables V. and VI.

The amount of dried blood added to the Norfolk fine sandy loam is far in excess of the amount ever used in good agricultural practice. However, this amount was found to be necessary in order to obtain accurate analytical results, and to assure differences of a large enough order between the various samples of soil analysed; furthermore, it seemed desirable to add enough dried blood protein to the soil to render the small amount of soil proteins negligible, so that only the fertiliser nitrogen would be under observation. By reference to Table III., in which the results of the analysis by the Van Slyke method as applied to the mixture of blood and soil are reported, it will be observed that the figures obtained for the various forms of nitrogen correspond very closely to those obtained from the dried blood alone, except the figures for melanin and non-amino nitrogen, but the reason for this is not altogether clear.

Ammonia Formation.

Assuming that ammonification of protein material in soil must precede nitrification and denitrification and that

TABLE VI.—Forms of Nitrogen in the Soil at the End of each Period. Hydrolysable Nitrogen at the End of each Sampling Period = 100.

Form of nitrogen.	Original soil.	Time in days from the beginning of the experiment.				
		18.	44.	86.	148.	240.
Amide	7'008	9'555	14'840	22'556	19'471	19'246
Melanin	4'767	6'375	10'773	9'453	7'657	10'910
Arginine	7'601	6'477	7'491	7'717	7'567	8'333
Histidine	12'366	16'276	13'663	12'099	13'421	12'006
Lysine	10'093	9'550	2'710	1'784	2'979	5'809
Monoamino acid	58'220	50'812	45'847	37'264	44'745	42'922
Non-amino	0'312	1'410	4'125	9'102	4'160	1'774
Hydrolysable	100'000	100'000	100'000	100'000	100'000	100'000

all loss of nitrogen in this investigation is due to ammonia evaporation, nitrification, or denitrification, and that free nitrogen is not split off from compounds other than nitrates or nitrites, then it is possible to arrive at the amount of ammonia formation in the soil during each period of time. It should be stated that this is ammonia formation exclusive of ammonia assimilation, there being no way in which ammonia assimilation could be accurately determined in these experiments.

This ammonia formation may be calculated by the following equations :—

Total N—NH₃ nitrogen in the original soil = A.

Total N—NH₃ nitrogen at the end of each period = B.

Then A—B = X, or ammonia formation during the period.

X/A = per cent of nitrogen changed to ammonia during the period.

In Table IV. are presented the results obtained by the use of these equations.

TABLE IV.—Per Cent of Total Nitrogen in the Soil Ammonified at the End of each Period of Sampling.

Time in days from the beginning of the experiment.	Per cent of total nitrogen.
18	18'72
44	54'03
86	72'66
148	78'13
240	78'92

The Results obtained by the Van Slyke Method.

By comparing the results obtained by the Van Slyke analysis of each soil sample during the experiment with the results obtained on the original soil the amounts of gain or loss in the eight different forms of nitrogen can be arrived at. It is thus possible to determine how rapidly any particular form of nitrogen compound disappeared from the soil during the course of the decomposition, and, further, to determine the relative amounts of nitrogen in these fractions in respect to the total amount of nitrogen present in the soil at the end of any period. When an increase in any particular form of nitrogen over the amount present in the soil during the previous period is observed, it is not possible in all cases to state the compound in which this nitrogen existed. But when a certain form of nitrogen shows a loss during a period it is an absolute indication that that particular kind of nitrogen was disappearing or had disappeared from the soil, although the rate could not be determined. The results obtained by this analysis are presented in Table V., in which the amounts of nitrogen in the various fractions are reported in percentages of the hydrolysable nitrogen of the original soil.

The figures presented in Table VI. represent the relative amounts of the various forms of nitrogen in percentages of the hydrolysable nitrogen of the soil present at the end of each period. From this table the fluctuating composition of the hydrolysable nitrogen of the soil may be followed, and the final composition of the hydrolysable nitrogenous matter of the soil may be established.

TABLE V.—The Forms of Nitrogen in the Soil at the End of each Period. Hydrolysable Nitrogen in the Original Soil = 100.

Form of nitrogen.	Original soil.	Time in days from the beginning of the experiment.				
		18.	44.	86.	148.	240.
Amide ..	7'008	7'515	6'025	5'429	3'454	3'222
Melanin ..	4'767	5'080	4'374	2'276	1'391	1'698
Arginine ..	7'601	5'162	3'041	1'857	1'342	1'395
Histidine ..	12'366	12'975	5'547	2'912	2'382	2'010
Lysine ..	10'093	7'610	1'110	0'429	0'528	0'972
Monoamino acid ..	58'220	40'493	18'612	8'970	7'938	7'187
Non-amino ..	0'312	1'120	1'675	2'191	0'738	0'297
Hydrolysable ..	100'000	79'660	40'598	24'070	17'740	16'741

The figures presented in Table VII. show the amounts of loss of nitrogen in each form from the soil at the end of each sampling period. The amount of loss is stated in percentages of the largest amount of any form of nitrogen in the soil at any time; for example, in the case of the amide nitrogen the amount is largest at the end of eighteen days, and this figure is taken as 100. In this table the word "gain" indicates an increase in the amount of nitrogen over that present at the end of the preceding period.

TABLE VII.—The Percentage Loss of the various Forms of Nitrogen in the Soil at the End of each Sampling Period. The largest amount of Nitrogen in the Soil in each Form = 100.

Form of nitrogen.	Time in days from the beginning of the experiment.				
	18.	44.	86.	148.	240.
Amide	Gain	20	28	55	57
Arginine	31	60	76	83	Gain
Histidine	Gain	58	80	82	83
Lysine	24	89	96	Gain	Gain
Monoamino acid ..	31	67	84	86	89
Hydrolysable	20	59	76	82	83

Hydrolysable Nitrogen.

During the 240-day decomposition of the dried blood in the soil a loss of 83 per cent of the total hydrolysable nitrogen took place. At the end of eighty six days the loss was 76 per cent, showing that during the latter and longer portion of the decomposition experiment the amount of hydrolysable nitrogen which vanished from the soil was extremely small.

Monoamino Acid Nitrogen.

During the experiment the monoamino acid nitrogen diminished from 58 to 7 per cent, or a loss of 89 per cent of the total monoamino acids originally present in the proteins. At the end of eighteen days 31 per cent of this form of nitrogen had vanished, while during the same time only 20 per cent of the hydrolysable nitrogen was lost. Since the monoamino acids contain more than half of the total hydrolysable nitrogen it would appear that the relative

loss from each would be about the same. The fact that there is a difference of about 11 per cent between the losses from these fractions leads to the supposition that nitrogen split off of the monoamino acids has been assimilated by the micro-organisms in the formation of their protoplasm.

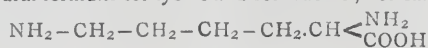
From Table VI. it will be observed that the proportion of the monoamino acids present in the soil at the various times of sampling fluctuates. The lowest figure is 37 per cent at the end of eighty-six days.

Lysine Nitrogen.

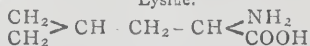
The analytical results show that lysine disappears from the soil quite rapidly. At the end of forty-four days 89 per cent of the lysine originally present in the proteins has been decomposed, and at the end of eighty-six days 96 per cent. During the remaining and longer part of the decomposition period there is a continual gain in lysine nitrogen, indicating that synthetic processes are at work.

The gain in lysine nitrogen, after the original had practically vanished from the soil, is to be attributed to the action of the micro-organisms in synthesising some compound or compounds which give the analytical reactions for lysine. That this increase is due entirely to lysine cannot be stated, but lysine no doubt makes up a part of the gain observed.

It will be noted from Table VII. that the two fractions which show the greatest amount of loss during the experiment are lysine nitrogen and monoamino acid nitrogen. It is not surprising that these two show the greatest loss when their chemical composition is considered. The monoamino acids are straight chain acids with the amino group in the α -position to the carboxyl group. Lysine, a diamino acid, is also a straight chain acid containing two amino groups, one in the α -position to the carboxyl group, and one at the extreme end of the chain from the carboxyl group, or in the ω -position. The relationship between lysine and the amino acids may be clearly shown by presenting the structural formulæ for lysine and for leucine; for example:



Lysine.



Leucine.

However, it is observed that the lysine vanishes more quickly from the soil than the monoamino acids. This may be due to the fact that the ω -amino group of the lysine exists free in the molecule of the native proteins which occur in the dried blood. Under such conditions this group is subject to deamination by the action of the micro-organisms before hydrolysis takes place, while in the case of the monoamino acids hydrolysis must precede deamination, since these acids are linked in the protein molecule in anhydride structure. Furthermore, if the ω -group be split off from the lysine while it is still a constituent part of the protein molecule it is changed into an amino acid with but one amino group, and would be determined analytically as monoamino acid nitrogen.

From Table VI. it will be observed that there are very marked fluctuations in the proportions of lysine nitrogen in the soil at the end of each period. The lowest amount occurs in the soil at the end of eighty-six days, which was the low point for monoamino acids. The final amount is about half that originally present in the dried blood.

Histidine Nitrogen.

At the end of eighteen days the histidine nitrogen showed a gain. Although the compounds which cause this increase cannot be arrived at it is possible that they are, in part at least, the purine and pyrimidine bases, which by the analytical methods would be classed as histidine nitrogen. It is well known that the protoplasm of micro-organisms is made up of considerable amounts of nucleoproteins and nucleic acid, which on hydrolysis would yield the purines and pyrimidines.

At the end of forty-four days 60 per cent of the histidine nitrogen had disappeared, at the end of eighty-six days 80 per cent, and after 240 days 83 per cent.

The proportion of the histidine nitrogen in the soil at the various times of sampling is about constant, with the exception of the eighteen-day sample.

Arginine Nitrogen.

After eighteen days 31 per cent of the arginine had vanished from the soil, while at the end of 148 days 83 per cent had gone. From the 148th to the 240th day, a period of ninety-two days, a gain in arginine nitrogen is observed. This may be due to nitrogen in the form of arginine, or nitrogen in the form of compounds which give the analytical reactions for arginine. It is nitrogen formed by the action of micro-organisms, probably a synthesis of protoplasm, and possibly in the form of proteins.

The relative amount of arginine nitrogen shows little fluctuation throughout the experiment, and is a little greater at the end of the experiment.

Amide Nitrogen.

The analysis of the figures for amide nitrogen brings out some interesting points. After eighteen days there is an increase in amide nitrogen. It may be safely assumed that the compounds which this increase represents are acid amides formed by the action of the micro-organisms, existing in the soil either free or combined in the molecule of some new proteins contained in the protoplasm of the organisms. That there was actually an increase in this form of nitrogen after eighteen days was, however, unexpected, since it is well known that micro-organisms when grown in solutions of acid amides can use them for the building up of their protoplasm, and, furthermore, Jodidi (1912) has shown that acid amides are very easily and quickly ammonified when placed in an agricultural soil. It was therefore expected before the results were obtained that the amide nitrogen would be among the forms which would most quickly disappear from the soil. From Tables V. and VII. it will be observed that this fraction disappears least completely and most slowly.

The question arose as to whether the soil used was capable of ammonifying acid amides. Consequently, 1 gm. of pure asparagine, one of the two acid amides considered to be present in the protein molecule, was added to 100 grms. of air-dried Norfolk fine sandy loam to which no dried blood had been added. The soil was made to about a 10 per cent moisture content, and allowed to stand for four days. On analysis for ammonia it was found that the soil had converted 73.4 mgrms. of asparagine nitrogen into ammonia nitrogen in this time, or, in other words, the soil in four days had ammonified 39.3 per cent of the total asparagine nitrogen. This shows that if acid amides were free in the soil they would have been to a very large extent converted into ammonia during the eighteen days of the experiment, and points unquestionably to the fact that the increase in this form of nitrogen is due to the synthetic action of the micro-organisms in the building up of their own protoplasm.

Society of Chemical Industry.—The Committee and Members of the Chemical Industry Club invite all those members of the London Section who have not already joined the Club to attend its first meeting, which will be held on Monday, May 21, at 8 p.m., at Lyons's Birkbeck Café, High Holborn. An interesting programme has been arranged, and, in addition to other items, Mr. M. C. Lamb will read a paper on "The Commercial Utilisation of Discarded Army Boots and other Waste Leather." Mr. Lamb has undertaken the investigation of this matter at the request of the War Office. He will include in the paper the suggestions of other investigators. The object of this publication, which is being made at the express wish of the War Office, is to incite, if possible, discussion and the formulation of further suggestions for the utilisation of this waste product on a commercially profitable scale.

THE INTERNATIONAL MOVEMENT OF FERTILISERS AND CHEMICAL PRODUCTS USEFUL TO AGRICULTURE.*

THE unsatisfactory results afforded by the last cereal crops throughout the greater part of both hemispheres have induced Governments and other persons interested to seek for the means of obtaining better yields in the coming season, in order to minimise the risk of another deficient harvest. The judicious use of fertilisers is among the principal of these expedients; investigations as to their production and disposal therefore take rank as questions of the greatest usefulness.

The review now under consideration, which appeared in the March, 1917, number of the *Bulletin of Agricultural and Commercial Statistics of the International Institute of Agriculture of Rome*, deals fully with this subject.

It consists of more than seventy pages, and includes a considerable number of statistics, some official, some from other trustworthy sources. Phosphatic, potash, and nitrogenous fertilisers are dealt with, as well as the principal chemical products useful to agriculture.

We proceed to the résumé or reproduction of the most important items of information.

I. THE WORLD'S PRODUCTION.

Natural Phosphates.

It is noteworthy that the American production for 1915 indicates a decided decline.

While in 1913 the United States extraction of phosphates was 3,161,146 tons, the quantity made available in 1914 was 2,777,917 tons, both of these being about normal, but in 1915 the total fell away to 1,865,123 tons.

This decline indicates very clearly the difficulties encountered in this industry ever since the outbreak of war. A considerable proportion of the hands previously employed in the phosphate industry took up other descriptions of work which have been increasingly in demand for the past two years, with remunerative pay. On the other hand, the European demand has fallen off very decidedly as compared with the requirements in 1913 by more than a million tons. Shipment for central Europe, where the consumption was very large, have almost entirely ceased, and for other parts of this continent the traffic has not asserted itself very vigorously. Business has been interfered with by scarcity of steamers and advanced rates of freight.

Lastly, in regard to markets within the country itself, the large demand for sulphuric acid for war purposes has also been a factor tending to diminish the output of phosphates intended for the United States. The price of the acid has advanced so seriously that the manufacture of superphosphates in that country has fallen off to a marked extent.

Turning to the data of American shipments, we find that those of Florida hard rock were reduced in 1916 to such small quantities that they scarcely merit attention. It seemed probable in 1915 that the shipments then going forward would be the minimum for this trade, but the continued decline during 1916 indicates that the trade in this description of phosphate has become quite unimportant.

The chief reasons for this decrease in the traffic arise from the war. In 1916, less than 33,000 tons were placed on board ship, and of this 4600 tons were for destinations in the United States.

The decrease in the trade of land pebble phosphate was not quite so marked, though equally noticeable. In 1916 and in 1915, shipments to countries other than the United States were practically identical in quantity, but they both show a deficiency of nearly 700,000 tons as compared with the shipments of this description of phosphates effected prior to the war.

In North Africa, although excepting for Tunis we have no data as to production of phosphates in 1916, we can assume that a considerable increase is shown. While in 1915 exports were no more than 226,000 tons, they reached in 1916 a total of 380,000 tons, somewhat larger than those of 1914 with 355,000.

In Egypt, on the other hand, the exports of 1916 show a deficiency of over one-third as compared with those of 1915 (21,000 tons against 33,000), and these latter did not reach one half of the exports in 1914 (87,000 tons). For Tunis, also, though in a less degree, there has been some decline in exports in 1916, almost entirely due to the returns of the second half of the year. Production, on the other hand, was greater in 1916 than 1915. The Government of Tunis informs us that there are considerable reserve stocks.

It would appear that, among the deposits of the islands in the Pacific there has been considerable renewed activity. We hear from private sources in Japan that, since the beginning of 1916, imports of phosphates to the extent of 80,000 tons have taken place from Rasa, 70,000 from Ocean Island, and 30,000 from Argaur, making a total of 180,000 tons.

We embody in Table I. the principal figures recently to hand and published in the Review of the International Institute of Agriculture of Rome.

TABLE I.—Natural Phosphates.
(In Thousands of Metric Tons).

	1916.	1915.	1914.	1913.
United States	711	1865	2777	3161
Algeria	380	165	226	461
Egypt	21	82	71	104
Tunis	1695	1389	1443	2884

The figures of 1916 relate to shipments, excepting those for Tunis, which relate to production.

Superphosphates of Lime.

In all producing countries the production is at present much reduced. This is on account of the difficulties encountered by manufacturers in obtaining the raw material.

In France the quantity of sulphuric acid that remains at disposal of the makers of superphosphates is very much curtailed by the immense employment of this acid for munitions. On the other hand, there are considerable difficulties in securing supplies of phosphates, such as scarcity of freight room and congestion at ports and on railways.

The production of 1916 was only about 350,000 tons, while in peace times it had been approximately two million tons.

Nitrate of Soda.

During the second half year of 1916, the production showed a slight reduction as compared with the first half of the year, in opposition to the usual course prevailing in peace times. This reduction did not, however, prevent the output of the second half of the year from exceeding those of previous corresponding periods. From July to December, 1916, the production was 1,425,751 tons, while in 1913, when the second half of the year provided the largest figures on record, the output was 1,393,610 tons. For the corresponding periods in war time the figures were respectively 1,175,763 tons in 1915, and 984,550 tons in 1914.

Stocks on the Chilean coast did not reach more than 718,315 tons at the close of 1916, although the production during that year had distanced all previous figures, while at the close of 1915 these stocks were 789,700 tons, and at the end of 1914 amounted to 1,087,910 tons. It should also be borne in mind that on June 30, 1916, the stocks were 888,621 tons, and that this total was the largest on record for that period of the year. The quantity delivered for consumption during the last half of 1916 was also a maximum, and, in fact, in spite of scarcity of tonnage and continually advancing rates of freight, shipments amounted

* International Institute of Agriculture, Rome, April 30, 1917.

to 1,635,818 tons during the second half of 1916. In 1915 they were no more than 1,196,638 tons. Europe, the United States, and the other importing countries were all sharers in this increase.

For Europe and Egypt 957,772 tons were shipped from July to December, 1916, in place of 673,348 tons during the corresponding period of 1915. The United States also show a considerable increase in their consumption. Chile forwarded to them during the second half of 1916, 592,901 tons against 452,582 in 1915, an increase of more than 140,000 tons. It is the same with regard to the other countries, 85,146 tons during the second half of 1916, against 70,708 for the corresponding period of 1915.

Turning to deliveries, these amounted in the United States during the second half of 1916 to a total of 526,261 tons, against 323,206 in the Atlantic States, and in the Pacific States to 51,683 tons, against 37,559 in 1915, the second half always understood. Owing to the present conditions it is impossible to ascertain the data of deliveries in Europe and in Egypt, but some idea of consumption may be deduced from the total arrivals. During the second half years these were for 1916, 700,199 tons, as compared with 480,825 for 1915.

Table II. is a summary of production and trade in Chilean nitrate of soda during the four years 1916, 1915, 1914, and 1913.

TABLE II.—Nitrate of Soda.
(In Thousands of Metric Tons).

	1916.	1915.	1914.	1913.
Production	2915	1764	2464	2774*
Export	2992	2031	1484	2740
Deliveries for consumption	730 (a)	861 (a)	2249 (a)	257
Visible stocks	718 (b)	790 (b)	1088 (b)	1772

(a) Incomplete data, owing to the circumstances.

(b) Chilean coast only.

Sulphate of Ammonia.

The British production of ammonia, calculated into sulphate of ammonia (including that used in the manufacture of ammonia soda, munitions, and for other chemical purposes) from all sources in the United Kingdom at 445,029 tons in 1916, against 432,836 tons in 1915.

The actual output in the United States for 1915 proved to be 199,581 tons, and that for 1916 is estimated to have been 291,835 tons; that is, 95,264 tons larger than for 1915. The particulars of origin of these productions will be found in detail in the special table for the United States. The output for 1916 is the largest yet furnished by that country. It appears from this fact that the home demand has been quite exceptional as regards coke and tar derivatives, as well as for ammonia for munition work. Imports into the United States were very small during 1916, on account of the British Government restrictions on all derivatives of oil.

Sulphur.

The Italian production has been diminishing for several years, owing to scarcity of capital, the closing of some large mines in consequence of fires, North American competition, the continual development of pyrites as material for sulphur manufacture, and lastly the partial stoppage of trade in sulphur for the last two years by reason of the war.

In the United States, although 1915 was a prosperous year in the sulphur trade, the production was below that of 1914. During the earlier portion of the year business was dull, but became more active towards the close.

Exports in 1915 were only 49,168 tons of sulphur, against 111,787 in 1914, in spite of the partial stoppage which the war caused in European trade. This reduction in American exports is chiefly due to transport difficulties, also resulting from the conflict. On the other hand, exports in 1916 exceeded 130,000 tons.

TABLE III.—Sulphate of Copper.
(In Thousands of Metric Tons).

	1916.	1915.	1914.	1913.
France	27	16	21	26
Great Britain	60	66	69	77
Italy	48	50	31	44
United States	—	19	14	25

TABLE IV.
(In Thousands of Metric Tons).

	Years.			Last six months.		
	1916.	1915.	1914.	1916.	1915.	1914
Natural phosphates.						
Importing countries*—						
Spain	288	212	202	176	132	111
France	286	326	661	139	168	189
Great Britain	339	381	571	198	225	292
Italy	419†	457	514	181†	206	266
Japan	90†	136	285	55†	56	94
Basic slag.						
Importing countries—						
France	1	10	34	0	1	7
Great Britain	0	0	17	0	0	3
Italy	3†	1	23	2†	1	18
Exporting countries—						
France	4	4	237	3	1	7
Great Britain	39	119	134	23	48	64
Superphosphate of lime.						
Importing countries—						
Spain	23	64	117	15	46	82
Russia	0	0	122	0	0	36
Exporting countries—						
France	12	60	117	4	39	45
Great Britain	15	70	67	6	25	39
Sweden	0	18	42	0	0	9

Salts of potash.

Importing countries—						
France	0	1	42	0	0	1
Italy	1	2	10	0	0	5
United States	4	254	1203	1	4	187

Nitrate of soda.

Importing countries—						
France	541	254	297	284	187	64
Great Britain	21	134	175	13	26	108
United States	1238	586	735	596	447	249
Exporter—						
Chile	3185	2029	1846	1821	1194	643

Sulphate of ammonia.

Importing countries—						
France	25	11	9	9	4	1
Italy	3†	8	13	0	1	7
United States	13	58	76	3	10	35
Japan	7†	20	106	4†	6	42
Exporter—						
Great Britain	263	318	328	134	136	151

Sulphur.

Importer—						
France	117	99	116	42	46	33
Exporting countries—						
Italy	318†	394	258	87†	194	63
Japan	71†	75	52	29†	49	34

Sulphate of copper.

Importing countries—						
France	21	34	24	7	10	2
Italy	6†	14	22	0	1	0
Exporter—						
Great Britain	39	66	69	14	15	6

* For exporting countries see Section I.

† Data incomplete.

The export of sulphur from Japan has recovered since the outbreak of war, for the foreign demand has increased

and prices have gradually risen. The greater proportion of Japanese sulphur is forwarded to the United States and to Australia, while some is shipped to Canada and to India. Formerly, shipments to Europe were on a very small scale, but since the war began the export from Europe to the East has almost ceased, while the European demand has increased. Japan will doubtless profit by these favourable circumstances.

Sulphate of Copper.

We summarise in Table III. the figures published by the Institute.

II. INTERNATIONAL TRADE.

So long as the war lasts, international trade in the products under consideration continues to decrease considerably, with the general exception of Chilean nitrate of soda, and partial ones in respect of a few special trades. This decline is the result of scarcity of tonnage and very high rates of freight, together with restrictions on exports and prohibitions imposed by Government owing to the part played, to an extent more or less important, by these products in the manufacture of munitions of war.

On the other hand, trade in nitrate of soda has gone on increasing considerably, both for Europe and the United States.

III. WHOLESALE PRICES.

Generally speaking, the rise in prices of fertilisers—including sulphur and sulphate of copper—has not ceased to operate, but the strength of the advance has diminished owing to Government intervention, resulting in maximum prices being fixed in many countries, and to very considerable fluctuations in price on sundry markets.

Quotations of the principal products for the most important markets are given in Table V.

TABLE V.—Average Price for the Year 1916.
(In Gold Francs per Metric Quintal of 100 kilograms.).

	July.	December.	Second half.	For the year.
Chlorate of potash.				
London	138.72	136.49	137.23	137.81
Genoa	82.24	n. q.	81.03	87.11
New York.. ..	159.44	237.11	199.95	207.15
Sulphate of potash.				
London	151.33	148.90	148.25	146.32
Genoa	57.02	n. q.	57.58	55.13
New York.. ..	149.80	149.82	149.82	163.15
Nitrate of soda.				
Valencia	48.70	56.19	50.75	48.85
French Atlantic ports	41.75	45.45	42.26	40.22
Genoa	41.63	60.12	47.05	43.90
Liverpool	46.66	47.65	45.34	44.35
New York.. ..	36.24	36.59	35.39	37.47
Sulphate of ammonia.				
Valencia	59.64	69.40	59.56	56.87
Paris	51.01	54.16	51.58	50.51
Genoa	51.49	49.11	50.22	50.84
Hull	43.32	44.08	44.12	43.15
New York.. ..	41.14	50.89	42.76	43.43
Crude sulphur.				
London	22.45	28.54	25.71	23.12
Licata, Sicily	14.33	18.19	16.31	13.63
New York.. ..	18.23	18.24	18.24	16.57
Sulphate of copper.				
Valencia	203.79	157.33	181.15	189.94
French Atlantic ports	138.95	138.79	137.49	127.50
London	127.12	160.80	136.49	130.31
Genoa	n. q.	n. q.	141.16	143.78
New York.. ..	204.25	145.90	163.20	187.06

NOTE. - n. q. = no quotation.

In addition to information already mentioned, and including only a very small portion of the review published by the International Institute of Agriculture of Rome, this review comprises interesting reports on German potash salts, on French sulphate of copper, on the production of fertilisers in the United States, on the use of fertilisers in Russia, the Union of South Africa, Australia, and Hawaii. It concludes with a bibliography of 457 notices of the literature relating to this subject which appeared during the last six months of 1916.

EMPIRE TRADE NOTES.*

Organisation of British Engineering.

A FURTHER stage in the formation of plans for the furtherance of British engineering interests after the war is marked by the decision of the British Engineers' Association to affiliate to the British Empire Producers' Organisation, which now represents an aggregate of over £500,000,000 of invested capital. The British Empire Producers' Organisation has exceedingly powerful connections amongst associated industries of the Dominions and Colonies concerned with both agricultural and manufacturing production, and it is, of course, largely to such markets, many of which are largely undeveloped, that British makers of machinery and rolling-stock must look in the future for the prosperous maintenance of their business. The stoppage of munition work at the end of the war will release an immense capacity of engineering production which may find employment temporarily in restoration work following the ravages in the battle-field areas, but which for more permanent business success must depend largely on the vigorous development of Empire territory, involving much railway and harbour construction and the application of enormous quantities of machinery of all kinds. The reciprocal advantages of an alliance between the great overseas producers and the British engineering manufacturers are therefore obvious.

The Coming of Coal Economy.

Warnings have reached the Government from more than one of the influential committees appointed to report on trade re-organisation, as well as from war productive departments, that it is essential to general industrial efficiency that there should be an overhauling of our methods of public distribution of electricity. The question concerns, on the one hand, the conservation of our stocks of coal and the avoidance of waste in its consumption, and, on the other hand, the supply of power by wire at the cheapest possible rates to all classes of manufacturers, and as soon as possible also to the agricultural industry. It is regarded by the British Empire Producers' Organisation as one of the most vital changes that must be made for the sound economic development of the country that there should be no vested interest obstructions left between the coal mine and the consumer's switch-board. At the present time the great majority of our manufacturers are paying at least twice as much for their power as they would be if the whole system were reorganised on a scientific basis, and at the same time the rich chemical contents of many millions of tons of coal are being lost. It is, of course, not possible to arrive at perfection by one step, but it is advantageous to have a clear conception of what technical development can do for the country as soon as the politician and the financier are prepared to come into line. The engineer has been kept waiting for them far too long.

The coal deposits of Britain, properly exploited, will

* Issued by the British Empire Producers' Organisation, Kingsway House, Kingsway, London.

play a very important part in economic reconstruction. The right way of using them for our own industrial and domestic purposes is to restrict the consumption of coal on the old system as much as possible and to encourage the concentration of heat, light, and power supply at large generating stations which will not only burn the coal to generate electricity, but will at the same time extract from it by distillation all the valuable by-products now so much better appreciated since the special demand has arisen during the war in regard to explosive and fertilising materials.

The Romance of Indigo.

This year's crop of Indigo is estimated in India at a value of £6,500,000. Before the war the figure had declined to less than £100,000. The area under cultivation has increased during the war from 148,000 acres to over 600,000 acres. It is therefore of very vital interest how far the return of peace will bring with it a renewal of the German artificial dye competition, and the Indian planters have been in conference with the British Empire Producers' Organisation on this important question of industrial development. Study of the pre-war conditions is bringing to light some remarkable and curious features. Most surprising is the fact that many people of "scientific" attainments appear to have accepted without question the claims of superiority on behalf of the artificial substance. That it was German and that it was "synthetic" seemed in those times a sufficient warranty of its being the last word in scientific achievement, and even the British Navy was converted by hypnotic suggestion in the same way. Now it appears that what came in the form of "synthetic" indigo from Germany, at an amazingly low price, was for the most part merely alizarine blue, and not indigo at all. It dyed things blue, but not so as to stand long exposure to sun and salt water. The one commercial advantage offered was cheapness and preparation in convenient packet form, the larger cakes of natural Indigo requiring the skilful use of machinery. It is hoped that as the result of current experimentation this difficulty may be shortly overcome and the material be presented in the form of a paste of even quality. The cost of producing natural indigo is, of course, much lower than that of making "synthetic," and there appears to be room for much further research in the commercial utilisation of the crop.

War and Trade in America.

Anxiety is expressed by some American trade journals at the prospect of international commerce under British Imperial preference, with differential terms to our Allies. The British Empire and the United States are the two World Powers that are almost completely self-contained in respect of essential material wealth; but of the two our own Commonwealth has the greater variety of production, while the United States has the advantage of enclosure within a great continuous stretch of territory and a wonderfully efficient transportation system. In the opinion of the British Empire Producers' Organisation there is ample room for the economic progress of both with benefit to the whole world. It is not in a merely competitive spirit that our Empire should be industrially developed. It is our duty to humanity that its boundless treasures should be vigorously and scientifically produced, and it is by such action that we can best play our part in the rapid restoration of prosperity amongst those nations which are freely sacrificing men and money to lay the foundation of a lasting peace for all mankind.

That is the best answer to such statements as this typical extract from a recent issue of the *American Metal Market Report*:—

At the Paris Economic Conference held last year all the Allied Governments were pledged to a policy of mutual protection in future tariffs, which is to take the form after the war of tariffs that will maintain preferential duties on goods interchanged among the Allies and

their colonies. The British colonies are very aggressive in advocating this policy, and the sacrifices they have made in this war in sending nearly a million of their best young men to the front will make it a matter of Imperial necessity for England to adopt the preferential policy after the war. . . . An adverse balance of trade has eaten up a large share of the income which England has obtained in the past from foreign investments. The enormous war debt will force England into an Imperial policy to conserve this income by restricting imports from foreign countries and substituting colonial products for materials obtained from foreign sources. England will become vastly richer under this policy, because it will force the development of enormous resources within the Empire which have been lying dormant. Canada is an example of what may occur in other colonies. A century ago Canada was just as rich in natural resources as it is to-day, but it was a wilderness with a little fur trade. The same aggressive spirit that has changed Canada from a wilderness into a modern nation will work miracles in other colonies and parts of the Empire. The Canadian policy of preferential duties will very likely be carried to a higher level against American goods, supported by the intense imperial spirit that has been created by the war. Where will the American manufacturers find markets to replace what we are likely to lose by this policy?

The Wealth of Mesopotamia.

It is understood by the British Empire Producers' Organisation that it is the intention of the Indian Government to proceed promptly and vigorously with the economic development of Mesopotamia. It was one of the drawbacks of Turkish rule that the natives were discouraged from cultivating this extremely rich and fertile territory by the fact that when they had brought production to a certain stage the property was on one pretext or another taken away from them. With safe tenure and with irrigation and transport improvements Mesopotamia can very soon contribute much more largely to the world's food stock. In connection with these plans it is expected that the general re-organising of the administration of Bagdad will also be pushed forward, and this will probably include the early installation of an electric light, power, and tramways scheme. It is on all grounds highly important that the immense possibilities of economic expansion of this ancient city should be realised without delay.

The Power Famine.

Four municipalities competed for permission recently to commandeer big turbo-generating plant under construction for the fulfilment of an order from overseas. The sets were of 12,500 electrical horse-power each, and it is significant that the city which has succeeded, with the authority of the Ministry of Munitions, in obtaining these great machines has hitherto been regarded as only a second or third-class town. It is one, however, which on the demand of war work has increased its output of electrical energy by many millions of units, and will now again double this quantity by installing plant costing about £400,000, the power production of which is wanted for the manufacture of steel.

It is significant again that new plant of this character can be installed at a cost of from £12 to £15 per kilowatt, as compared with a general average throughout the country of an accumulated capital expenditure of about £45 per kilowatt. On the one hand there is an insatiable demand for cheap power, and on the other a great aggregation of antiquated generating plant. To modernise the electric power supply of the United Kingdom will, in the opinion of the British Empire Producers' Organisation, tax the entire capacity of the electrical manufacturing industry after the war, and if any export trade is also to be sought there must be great extensions of factories.

THE
CO-EXISTENCE OF MATTER AND ENERGY.

By FRANCIS A. DUGAN.

CHEMISTRY now is merely in the age of the Electron Theory and, viewed from the present-day theories, may be considered to have passed the period where the elementary nature of a substance was the final reference point. Now, to a limited extent if need be, we can tell the composition of the element itself. This we say, as we have evidence strongly supporting the theory that the atoms of all elements are composed entirely of a like unit of matter, and while we know nothing, other than conjectures, relative to the arrangement or numerical grouping of the unit composing the atom, still we know the unit and we think we know its composition. This unit is the electron and its composition is energy.

As a unit of matter the electron is considered the ultimate one, and is said to be composed entirely of what is termed a charge of negative electricity, which, we know, is regarded as energy and nothing else.

Energy as negative electrification, is capable under some unknown conditions of assuming a material form and of assuming a material action, as the electron, besides possessing mass, possesses the property of inertia.

Previous to the introduction of the electron theory, both of these properties were attributable to matter only.

Positive electricity is materially unknown, that is, it is not known to be capable of possessing mass as does the negative form, but it is, nevertheless, considered present with the negative form in the atom, or group of electrons, as we cannot think of one without association with the other.

The atom of any element is, according to the electron theory, considered as being composed entirely of electrons which are negative charges of electricity existing and, as some assume, revolving in a field of positive electrification.

According to this theory all differences in our elements are attributed to a different arrangement, or to a different numerical grouping of the electrons contained in the atom.

Our elements are, therefore, different manifestations of energy. They may be regarded as nothing else if the electron theory is a truth, and if such is so, then there is absolutely no such thing as actual matter.

Therefore in reference to the ultimate composition of all matter, we can to-day refer it to energy and none can dispute this reference unless one thing is at fault, that is, unless our conception of energy is wrong. The undisputed fact that no energy is ever lost is not necessarily a positive proof that our conception of energy is correct.

I have good reason to believe that our conception of energy, or our views on energy, if that would be more in keeping with the facts, are not only at fault, but are entirely wrong. We cannot better understand matter by referring it to energy as we must admit that we do not understand energy itself.

What I consider we need most, at present, is a better understanding of energy, therefore I think a question in reference to energy should, at this time, be both pertinent and opportune.

If we are asked "What is actual energy?" we are obliged to answer that in reality we do not know.

What is our conception of energy? We have none, or at best none that amounts to anything of real value. True, we are acquainted with the convertibility of energy, but aside from that all we seem to know is that none is ever lost.

Aside from the fact that energy, in the electrical form, is now known to be capable of possessing mass, we have practically no knowledge of energy itself. We content ourselves with the observation of its results, and the results are the only means by which we compute it.

One cannot give serious thought to our conception of energy, and particularly to those modifications of recent

development, in reference to matter, without inferring that something is wrong.

For instance: If all matter is energy, and nothing else, then we must admit that the subdivisions of energy, in the electrical form, are at least as numerous as there are chemical compounds. This must be admitted even though they be numbered in the tens of thousands. A chemical compound, in its entirety, is different from everything else. Energy, therefore, in embodying all matter would, I think, be assuming too many forms to be in keeping with things natural. It would not harmonise with the simplicity of Nature. All things in natural science are simple—very simple—but sublime in their simplicity, and the path of true science must ultimately lead towards simplicity. The more it departs from this the more erroneous will be its teachings. Science's mission must be that of an explanatory and comprehensive nature and that which embodies both these is really simple in the end.

To say that all matter is composed of energy does not, in the least, simplify matter; in fact it does not give us as clear an understanding of it as we held heretofore, and, what is worse, it makes energy even more mysterious. Taking this view, I cannot consider the electron theory, relative to matter and energy, as at all scientific, as it confuses rather than explains, and it complicates instead of simplifying.

It is partly this which leads me to believe that we will be obliged to change our views in regard to energy before an explanatory definition of it can ever be presented.

If the present-day teachings are correct then actual matter does not exist; energy and changes of energy being the only things with which we are familiar.

Chemistry would then be, as many say, merely a branch of Physics, and Physics would be the science of the universe. Of course there is, and always will be, such a science as Chemistry. I do not present this paper merely through sentiment towards chemistry, nor solely to take a position directly opposite to the physical views of the present day, but simply to offer my efforts in an endeavour to arrive at a somewhat comprehensive idea of matter and energy, and to set forth what I consider to be the truth.

From the views I hold on matter and energy I cannot conceive of the possibility of an actual physical change, or that such a science as physics can exist, excepting, perhaps, that of a unit of matter moving at some definite velocity. I regard everything in Nature as being chemical and every change in the universe as being chemical in nature. Even the mere imparting of motion to a body I regard as a chemical change, as I consider it must cause a change in the mass of the body before motion can be imparted.

As this view is at variance with our accepted theories, and as I will later have occasion to mention others which are likewise at variance, I will at this stage make a few statements that I believe, so that through the reading of this paper there may be no doubts as to the points in question, or to the idea that I am endeavouring to convey. My beliefs are:—

First.—That there is but one form or species of energy in the universe.

Second.—That matter is an actual substance, but that it is linked inseparably to motion, thus furnishing the only form of energy capable of existing, namely, mass in motion.

Third.—That all matter is in motion and, unit for unit, is moving with equal energy or as the mass times the velocity squared.

Fourth.—That matter is capable of existing in a state much more dilute than a gas.

Fifth.—That our law of inertia is not an actual law, but only an apparent law.

Sixth.—That the electron is not the ultimate unit of matter, and, in fact, that an ultimate unit of matter, strictly speaking, can have no existence, and that matter itself must be capable of existing, in dilution, to the infinite.

Seventh.—That the basis of all chemical action is not

as we assume, of a purely electrical nature, but is one of motion; a relation of mass to velocity, as is electricity itself.

Eighth.—That we can change the mass of all objects, but in doing so we likewise change the velocity, one being a function of the other.

Ninth.—That no energy is ever lost, because all matter is moving with equal energy.

Tenth.—That there is no such thing as an accident or coincidence in natural science. For instance, if two objects resemble each other, no matter in what respect, the reasons for such similarity are as near to each other as is the condition of similarity, and further, if any one law is applicable to two different phenomena, the cause of each phenomenon is identical.

By an examination of matter and energy we can readily see if such views are at all reasonable, or if they may be tolerated from a scientific standpoint.

As a means of presentation I will briefly examine our three states of matter and likewise something we know and designate as energy and see what relation they bear to one another.

For convenience, in referring to the different states of matter, I will take an object with which we can associate our ideas; we, of course, however, need not entirely confine our ideas to such object.

I will take an object which we can say exemplifies matter in all the states that we know and in addition furnishes us with some manifestations of what we term energy.

An object which will answer admirably for such a purpose is a candle. Take one composed of stearic acid, which is admittedly a solid.

We will light the candle and we note that this is easily accomplished by the application of a flame.

We will observe now that the candle is burning brightly and while it burns we may make some inquiries into what we have actually accomplished. We may say that in lighting the candle we have supplied a small amount of energy, which is true, but it was energy of a certain intensity; its mere equivalent, in another form, would not accomplish this. It would tend to deform the candle.

We have added in energy a very insignificant quantity when compared to the total amount possessed by the entire candle, and in fact we have done much more than simply to supply a small amount of energy, we have disturbed an equilibrium, and now have matter passing from the solid to the liquid state, from the liquid to the gaseous state, and from the gaseous or liquid to what we know as light and heat or, as we term them, forms or species of energy.

In the candle we have many things playing important roles. We have matter existing in the three states—solid, liquid, and gaseous—and the only states in which we recognise matter as capable of existing. In addition to this we have some forms of energy, light and heat; these two are very apparent to our senses, but we might also say that there are others present which are not apparent at all.

Perhaps some may contend that electricity is also present, as the electrons that compose the atoms of the candle itself, and if so we also should add that chemical energy is present, but as to this we have no direct proof. In fact we have no direct proof that such a thing as chemical energy ever existed; it is never manifested in the least, and it is only when, as we say, it changes its form and reveals itself to us as heat or as electricity that we can detect it; nevertheless we assume, or have assumed its existence; it may be, however, that the electron theory or the ionisation theory has eliminated it, all chemical energy now being regarded as of an electrical nature.

If chemical energy has been eliminated from our consideration we have much for which to be thankful, as it simplifies somewhat our understanding of matter and energy, as there is one less form or species in which energy is capable of existing.

In the candle we also have what we term attractions at work, that is, the molten material is flowing down from

the upper edge to the base of the wick, gravity is acting, and directly contrary to this the same material is raising by virtue of the imbibition or capillarity of the wick. This material in motion possesses energy.

This matter flowing free to gravity may be regarded as energy of position, which it is, and need not enter into our discussion in reference to the energy possessed by the candle; nevertheless, the material moving is matter in motion and we also have other manifestations of the same form of energy present in the entire candle. For convenience I will term it mass in motion. All will admit this to be present in the solid, liquid, and gaseous states of matter.

In the gaseous state of matter we know that the molecules are moving very rapidly and diffusing into the atmosphere. In the solid state we say that the molecules are vibrating at a rate or velocity more or less fixed by the temperature of the body itself, and the more heat we apply the more rapid become the vibrations.

Regardless of what other forms of energy may be present in our candle, there is no question but that we have this one form or species—mass in motion—existing in each of the three states.

Mass in motion is, at the present day, our principal form of energy. It has to be, as we rate all other forms of energy by their capacity for doing work. It is, therefore, our standard form.

A peculiar thing in reference to this which is worthy of notice here, is that if we view matter from the present-day theories, which say that all matter is energy and nothing else, then the only means we have of computing energy is the relation it bears to itself in motion. Under such viewpoint it becomes more complexed, too much so, I believe, to be correct.

We can observe in the solid state of matter—for example, the body of the candle—that in this state it coheres sufficiently to stand free and clear by itself, although its linear dimensions are quite a multiple of its diameter; it can therefore support weight, and while retaining its given conformations it is at the same time in motion.

We note that matter in this, as in other states, is capable of receiving heat, and in the case of the candle, is continually receiving heat from the flame; that is a latter portion of the candle is receiving something from a former portion of itself. Something is passing away but sufficient is remaining or being transformed into energy of a certain intensity which we call the flame, existing locally at the wick, and thus combustion ensues. Whatever heat may be it certainly has a strong bond in common with matter, as it is readily received by the solid state and at a certain point actually absorbed and disappears as heat, or becomes latent. I believe we have sufficient evidence here to say that if heat is merely a form of energy and nothing else, then a great portion of our candle consists of energy—simply energy—and nothing else.

If, however, we examine other things present and the properties they possess we must feel that we are not completely justified in making such a statement, as it might be possible to assume that heat is something more than energy, or our thoughts will, at least, lead us in that direction.

The solid state of matter when it receives the necessary quantity of heat which is common to its mass, undergoes a great change: it melts and gives us the liquid state of matter. This liquid state we can notice flowing down to the base of the wick. Matter in this state, as we know, is very mobile, it does not cohere sufficiently to stand superimposed like the solid, but readily flows, or tends to equalise its mass towards gravity, and if we wish to retain it we must use some vessel composed of solid matter. A cup shaped vessel is satisfactory. We have such a vessel at the base of the wick; it is composed of the same material as our liquid, but in a different state.

Matter in the liquid state must possess a greater vibratory motion than it did in the solid; this is conceded and this I consider a reason for its lesser property of cohesion.

We can notice from our three states of matter that the greater the velocity the lesser the cohesion. If we revert to the solid state we may use our candle to illustrate. We will examine the solid or lower portion which is cool. We can notice by pressing it with the finger that it possesses marked cohesion. If we proceed towards the flame we reach the warmer portions where cohesion is much less, and at the edge near the flame we can observe that our solid is easily deformed by a slight pressure of the finger. This portion is warmer and it is, as we know, in a more rapid state of motion than the cooler or lower portion and its cohesion is much less.

When the warm or plastic portion receives sufficient heat it melts, and here we have ocular evidence of vanishing cohesion, therefore the change of cohesion at this point is great. That being the case it is reasonable to assume that the change of velocity at this point must likewise be great.

To be continued.

CORRESPONDENCE.

BRITISH STANDARDS WEIGHTS AND MEASURES *v.* METRIC OR DECIMAL SYSTEM.

To the Editor of the Chemical News.

SIR,—Now that the London Chamber of Commerce, the Decimal Association, and kindred institutions, as well as individuals, have submitted their case for abolishing the existing British coinage, weights, and measures in favour of the metric or decimal system, we think it right to point out that there is a large body of responsible opinion which is strongly opposed to such a change, and for the following reasons:—

We do not contend that the maintenance of the existing British system does not involve certain disadvantages to the user, though they are almost entirely restricted to foreign commerce. These disadvantages, however, are mainly due to the fact that in dealing with countries where the decimal or metric system is in force difficulties have arisen in working the two systems in combination. These difficulties have been greatly exaggerated, and are for the most part of a purely arithmetical character, yet undoubtedly they exist, and it is by reason of them that a demand has arisen for some change which will avoid, or at least minimise, them.

Those who are in favour of such a change argue that the only possible course to adopt is to abolish by legislation the existing British standards, weights, and measures, and to substitute the metric or decimal system, which, as should be well known, has its own inherent defects and limitations, even when compared with our own.

The difficulties involved in such a course are admitted to be great, even by those who advocate the change. The cost to the nation would be enormous, and, while involving all businesses, would benefit mainly the largest and those engaged in foreign trade. The time necessary to bring into operation so far-reaching a revolution would be considerable. On the conclusion of peace, trade, and especially foreign trade, will call for the highest energies of this country, and the nation which is most ready to resume foreign commerce will stand to gain proportionately. To select such a time as this for inaugurating so far-reaching a change, with its inevitable scrapping of our existing system of bookkeeping, weights, and measures, would be an act of doubtful wisdom, even if the ultimate necessity could be proved up to the hilt, and there were no alternative course to adopt.

Fortunately for the interests of this country this is not the case, and it is possible at the same time to maintain our existing system while bringing its use into harmony with the requirements of foreign trade, and at last enabling commercial men in this country to compete on equal terms with their continental concurrents.

The adoption of such an alternative has been rendered possible by a simple and ingenious method, which enables anyone in buying, selling, or cataloguing to calculate British prices in any foreign currency, weight, or measure, or *vice versa*, by the simple multiplication of the price by one factor. The principle applies to every calculation, no reference or knowledge of the difference in weights, measures, and currency being required. Moreover, it is equally applicable to every country in the world, so that foreigners can adopt it with equal facility. The necessary tables are being revised and checked for publication, and will be ready shortly.

It is impossible in so brief a summary to set out all the advantages of this method, but we would refer you to articles which appeared in the *Investor's Review* of February 17 and March 17, 1917, reprints of which may be obtained on application to us. We shall also be pleased to arrange, by appointment, for a short demonstration to anyone interested, and we undertake to prove our contention that this "simple method" meets all requirements for foreign trade in all parts of the world, both in buying and selling. It will be ready for immediate adoption, and, while bringing about a much needed and long deferred reform in our commercial relations, it dispenses with the necessity of scrapping our present system, with all the attendant loss, expenses, and dislocation of business involved. It is emphatically our conviction that this "simple method," when known and understood, will be welcomed as eagerly by men of affairs as Napier's logarithms were three centuries ago by men of science.—We are, &c.,

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May 10, 1917.

MISCELLANEOUS.

Royal Society.—The Croonian Lecture, on "The Excitation Wave in the Heart," was delivered by Dr. Thomas Lewis on May 3.

Royal Institution.—A General Meeting of the members of the Royal Institution was held on the 7th inst.; Sir James Crichton-Browne, Treasurer, in the Chair. Lady Bax-Ironside, Sir John Stirling Maxwell, Bart., and Miss Helena Mond were elected Members. The special thanks of the members were returned to Miss Edith Hipkins for her present of the valuable Musical Collection of Books and Pamphlets by the late Dr. Alexander J. Ellis, F.R.S., M.R.I., and bequeathed to the late Dr. A. J. Hipkins.

Institute of Chemistry.—At a meeting held at the Institute of Chemistry on April 27, the President and Council presented a silver rose bowl to Mr. Richard Bertram Pilcher, Registrar and Secretary, in appreciation of twenty-five years' faithful service. The meeting was well attended, and the presentation was made by the President, Sir James Dobbie, Principal of the Government Laboratories. Mr. Pilcher, who joined the staff of the Institute as clerk in 1892, was appointed Assistant Secretary in 1894, Secretary in 1895, and has held the joint offices of Registrar and Secretary since 1900.

MEETINGS FOR THE WEEK

TUESDAY, 22nd.—Royal Institution, 3. "Architectural Design in Organisms—The Laws of Growth and Form," by Prof. D'Arcy W. Thompson, C.B.

THURSDAY, 24th.—Royal Institution, 3. "The Chromosome Theory of Heredity and the Alternatives," by Prof. W. Bateson.

FRIDAY, 25th.—Royal Institution, 5.30. "Breathlessness," by J. Barcroft, F.R.S.

Physical, 5. "Investigation of Radium Luminous Compound," by C. C. Paterson, J. W. T. Walsh, and W. F. Higgins. "Resistance to the Motion of a Lamina, Cylinder, or Sphere in a Rarefied Gas," by F. J. W. Whipple. "Effect of Stretching on the Thermal and Electrical Conductivities of Wires," by C. H. Lees.

SATURDAY, 26th.—Royal Institution, 3. "The Electrical Properties of Gases," by Prof. Sir J. J. Thomson, O.M.

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THE CHEMICAL NEWS.

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THE

DETINNING AND ANALYSIS OF TIN PLATE.

By GEORGE W. HEISE and AMANDO CLEMENTE.

Introduction.

PRACTICALLY all the tin plate on the market is made by a hot-dip process—by immersing carefully clean sheet iron in a bath of molten tin. The coating formed by this process varies from almost pure tin at the outer surface of the plate to a tin-iron alloy rich in iron near the surface of the iron base. Often varying amounts of lead are used in the molten bath.

The removal of the coating from tin plate, both for the commercial recovery of tin and for analytical purposes, has been the subject of much study. Among the commercial methods the most important are the electrolytic detinning in alkaline solution (Keith, U.S. Patent 176,658, 1876), the chlorine process (*cf. Electrochem. and Met. Ind.*, 1909, vii., 79), and various modifications of these (R. P. Skinner, "German Detinning Methods," *Det. Ind.*, 1914, xii., 236; "Detinning Industry," *Electrochem. and Met. Ind.*, 1909, vii., 79).

In addition a large variety of methods have been proposed, such as the mechanical separation of tin from tin plate by agitation of a mass of tin scrap with liquid air (W. J. Phelps, U.S. Patent 952,351, March, 1910); the treatment of the material with superheated steam (H. C. Wiltreck, German Patent 261,522, February, 1912), whereby tin is fused and loosened by the formation of iron oxides; solution of tin in strong commercial hydrochloric acid, kept cold to prevent the solution of iron (J. M. Calmels, French Patent 448,004, September, 1902); removal of tin by a solution of sodium plumbate (A. S. Ramage, *Met. and Chem. Eng.*, 1911, ix., 219); or electrolysis in a bath of phosphoric acid (A. E. Battle, British Patent 14,514, June, 1914).

Many processes have been recommended for the removal and determination of tin and lead in tin plate (*cf. H. Serger, Zeit. f. d. Untersuch. d. Nahrungs- u. Genussm.*, 1913, xxv., 465), among them the mechanical removal of the tin after heating over a Bunsen flame (*loc. cit.*); the digestion at boiling temperature with sodium peroxide (K. Meyer, *Zeit. Angew. Chem.*, 1909, xxii., 68), the difference in weight before and after treatment serving as an indication of the amount of coating; the solution of the tin coating in 12.5 per cent hydrochloric acid (Serger, *loc. cit.*), and subsequent precipitation of the tin as sulphide, heating, and final weighing as oxide; the solution in 10 per cent hydrochloric acid (H. Mastbaum, *Zeit. Angew. Chem.*, 1897, x., 329), precipitation with ammonium sulphide, and heating, after certain precautions, with ammonium carbonate; and the heating of tin plate with dry sodium peroxide (H. Angenot, *Zeit. Angew. Chem.*, 1904, xvii., 521), solution of the melt in water, acidifying with sulphuric acid, washing, heating, and weighing the precipitated oxide. I. H. Aupperle (*Metal. Ind.*, 1914, xii., 327) suggests (1) the solution of the tin in hydrochloric acid, with certain precautions, and the final determination of tin by titration with iodine solution, or (2) the removal of tin with concentrated sulphuric acid and the determination of the iron in the solution, the tin being obtained either by difference or by direct analysis as above.

The above methods either give merely the amount of tin present or else the total amount of plate (tin, lead, and iron alloy in the coating). If the amounts of tin and lead are desired additional processes are required.

Directions for a simple method for the determination of lead, as given by Serger (*loc. cit.*), are as follows:—

Take 0.1 grm. iron-free tin, carefully scraped from heated tin plate, decompose with 3 cc. of concentrated nitric acid on a steam-bath, and evaporate to dryness three times. Add 10 cc. of water, allow to stand on a water-bath for ten minutes, filter into a 100 cc. flask, and dilute to the mark with distilled water. Shake well, use 10 cc. in a large test-tube, and add 10 cc. of fresh hydrogen sulphide water. Compare the colour obtained with a standard made by adding 2, 5, 10, and 20 drops of a water solution, containing 0.16 grm. of lead nitrate per 100 cc. (1 cc. = 0.001 grm. metallic lead) to 10 cc. of water, and 10 cc. hydrogen sulphide water.

For rapid practical tests, where many examinations must be made to determine the quality of a large shipment of tin plate, simple determinations of the amount of coating per unit area will doubtless be found sufficient in addition to tests on uniformity of coating. Many of the procedures outlined are unnecessarily tedious.

In most of the foregoing methods the amount of iron alloyed with the tin is not determined, although it appears obvious that it is a factor having an important bearing on the quality of the resulting tin plate. A method which will first remove the coating, including the tin-iron alloys, from tin plate, and which will enable the subsequent determinations of at least the tin and iron in the coating ought to yield more valuable information concerning the quality of tin plate than a determination of the tin only, or of the tin and lead in the coating.

The work here recorded was done for the purpose of studying and developing methods of removing tin from plated iron without attack on the iron base, with special references to the analysis of tin plate.

Experimental Part.

Different brands of tin plate were used in the work here recorded, but none of these contained lead. A sample of tin plate of uniform appearance and apparently good quality was cut into squares 5 cm. on a side, cleaned with alcohol and ether, and analysed according to the method of Aupperle (*loc. cit.*), the final titration for tin being made with iodine solution. The results with different squares are given in Table I.

When stripped by immersion in boiling sodium peroxide solution (Meyer, *op. cit.*) samples of the same tin gave the results in Table II.

The Meyer method gives concordant and reliable results, but it is clumsy, because of the unavoidable and disagreeable spattering attendant on the use of sodium peroxide, and because long and repeated treatment is necessary to ensure complete removal of the coating.

The results obtained by this method are higher than those obtained by direct analysis of tin, the difference (about 0.05 grm.) representing the amount of iron removed with the tin plate. That this iron is actually part of the alloy and is not due to attack on the base is shown by the fact that there was no further loss in weight on subsequent treatment with sodium peroxide.

Since iron is an insoluble anode in certain alkaline and oxidising solutions, other metals can readily be stripped from it electrolytically (*cf. C. F. Burgess, Trans. Am. Electrochem. Soc.*, 1903, iv., 31). For the work here recorded a 30 per cent solution of sodium nitrate was employed as stripping bath, and the plate was made the anode. As will be seen the results obtained are comparable with those obtained with sodium peroxide. Comparable results were obtained with sodium or potassium hydroxide solutions, but with these the action was so slow that their use is not recommended. (See Table III.)

This procedure offers an extremely simple and rapid method of analysis. Stripping is accomplished in a few minutes. There is no danger of attacking the iron of the base. The iron of the alloy removed from the plate is left in the bath in such form that it can be readily recovered as ferric hydroxide, and can be determined quantitatively.

By reference to the results obtained in Table II. it is evident that the two methods are strictly comparable.

In a study of the stripping of galvanised iron, we called attention to a number of salts which would be replaced in solution of metals by zinc but not by iron (*Phillipine Journ. Sci.*, A, 1916, xi., 144). As zinc is generally electro-positive to iron in aqueous baths, metals intermediate in the potential series to zinc and iron should form salts which strip zinc from iron. Such salts were readily found, among them a number which might have been expected to attack iron as well as zinc. To find salts which will strip tin from iron is more difficult, since tin is electro-negative to iron in many aqueous solutions, and salts which dissolve the former might naturally be supposed to attack the latter.

Basic lead acetate solution will strip zinc from iron (W. A. Patrick and W. H. Walker, *Journ. Ind. and Eng. Chem.*, 1911, iii., 239), but leaves tin plate unattacked. Lead acetate does not affect tin plate either in neutral or (acetic) acid solution, but lead acetate or other lead salts, in solution made alkaline with sodium or potassium hydroxide, strip tin from plated iron very rapidly, depositing lead in a spongy easily removed condition. The accuracy of the method may be judged by the tests made on samples of the same tin plate previously analysed. (See Table IV.).

These data are again comparable with those obtained by the methods previously outlined. Concordant results are obtained, and unless great refinement is desired the method is sufficiently rapid and accurate to serve as a reliable guide in the judgment of tin plate. Compared with the data previously recorded the results obtained with alkaline lead acetate solution are a trifle low, showing that all of the tin-iron alloy is not removed immediately by this method. As a matter of fact, the lead solution does strip nearly all of the iron-tin alloy from the iron if the time of immersion is prolonged, the reaction being practically completed after an hour or two. Doubtless the presence of much lead in a tin coating would lessen the accuracy and applicability of this method.

Other salts of lead yield similar results, but the reaction is by no means confined to lead salts. Aluminium nitrate, made alkaline with sodium hydroxide, will strip tin, although the action is extremely slow. A solution of copper sulphate and tartaric acid, made alkaline with sodium hydroxide, has a similar effect. Chromium nitrate solution attacks both tin and iron, but the same solution with enough sodium hydroxide added to make a clear liquid will dissolve only the tin. The data secured with typical solutions are given herewith, the tables showing the results obtained with two different samples of tin plate. Lead salts are the only ones listed to be recommended for analytical work. (See Table V.).

Concentrated nitric acid will remove tin without attack on the iron base, although it will entirely destroy a piece of galvanised iron. Both tin and zinc are anodic to iron in concentrated nitric acid, and zinc is anodic to tin.

The experiments in Table V. are of interest, not only because of the apparent "reversals" of potential of tin, but also because of the fact that many of the reactions recorded took place in alkaline solutions in which the metals used (chromium, aluminium, lead, &c.) are generally thought to be part of the acid radicals.

Amount of Iron in the Coating.

The amount of iron alloyed with tin depends on the temperature and purity of the plating bath, and doubtless varies with different brands of tin plate. It is reasonable to suppose that it should be an important factor in determining the quality of tin plate and its resistance to corrosion. The various brands analysed by us showed iron contents in the tin coating of about 0.05 grm. per square decimetre.

Size of Samples to be used for Analysis.

The analytical data previously recorded indicate the lack of uniformity of coating to be expected in commercial tin

plate. Although errors are undoubtedly caused by failure to cut samples of tin plate accurately to squares of the required size, it is apparent that great discrepancies in uniformity of coating exist, even in samples cut from the same sheet. Obviously more concordant results would be obtained if larger samples were used, but in that case the analyst might easily fail to detect local defects in the coating. With the methods outlined, squares 5 by 5 cm., or at most 5 by 10 cm., should be ample for analytical purposes and should yield more reliable data than larger samples.

TABLE I.—Analysis of Tin Plate by Aupperle Method (Titration with Iodine Solution).

(Size of plate, 5 by 5 cm.).

No.	Weight of sample. Grms.	Weight of tin. Grm.	Weight per unit area.		Tin in tin plate. Per cent.
			Per square decimetre. Grm.	Per square foot. Ounce.	
1.	4.340	0.064	0.256	0.084	1.48
2.	4.340	0.072	0.288	0.094	1.66
3.	4.293	0.068	0.272	0.089	1.58
4.	4.330	0.071	0.284	0.093	1.64
5.	4.354	0.064	0.256	0.084	1.47
Average	4.331	0.068	0.271	0.089	1.57

TABLE II.—Analysis of Tin Plate by the Meyer Method. (Size of samples, 5 by 5 cm.).

No.	Weight of sample. Grms.	Loss after treatment.		Coating per unit area.	
		Grm.	Per cent.	Per square decimetre. Grm.	Per square foot. Ounce.
6.	4.346	0.082	1.89	0.328	0.107
7.	4.360	0.085	1.95	0.340	0.111
8.	4.289	0.078	1.82	0.312	0.102
9.	4.310	0.075	1.74	0.300	0.098
Average	4.326	0.080	1.85	0.320	0.1045

TABLE III.—Analysis of Tin Plate by Electrolysis. (Voltage, 3.5; ampère, 0.7; time, about ten minutes).
A. In a 30 Per Cent Sodium Nitrate Solution.

10.	4.346	0.082	1.88	0.328	0.108
11.	4.281	0.080	1.87	0.320	0.105
12.	4.261	0.079	1.85	0.316	0.104
13.	4.296	0.080	1.84	0.320	0.105
Average	4.296	0.080	1.86	0.321	0.105

B. In a 20 Per Cent Sodium Hydroxide Solution.

14.	4.337	0.072	1.66	0.288	0.094
15.	4.292	0.078	1.84	0.302	0.102

TABLE IV.—Analysis of Tin Plate by Immersion in Alkaline Lead Acetate (Sodium Plumbite) Solution.

(Five-minute test).

16.	4.285	0.078	1.82	0.312	0.102
17.	4.214	0.070	1.80	0.304	0.100
18.	4.221	0.072	1.70	0.288	0.094
19.	4.325	0.073	1.69	0.292	0.096
Average	4.261	0.075	1.75	0.299	0.098

(Three-day test).

16.	4.285	0.082	1.91	0.328	0.107
17.	4.214	0.082	1.95	0.328	0.107
18.	4.221	0.077	1.85	0.308	0.101
19.	4.325	—	—	—	—
Average	4.261	0.080	1.90	0.321	0.105

TABLE V.—*Detinning by Immersion.*

Plate A (size of samples, 5 by 5 cm., except as noted).

No.	Solution used.	Weight of sample.	Loss on immersion.		Weight of coating	
			Grms.	Per cent.	Per square decimetre.	Per square foot.
16—19.	Lead acetate and sodium hydroxide	4.261	0.075	1.76	0.300	0.098
20.	Lead chromate and sodium hydroxide	4.351	0.071	1.63	0.284	0.093
21.	Chromium nitrate and sodium hydroxide	4.401	0.067	1.61	0.268	0.088
22.	Aluminium nitrate and sodium hydroxide	4.321	0.065	1.52	0.260	0.085
23.	Copper sulphate, tartaric acid, and sodium hydroxide	1.224 (a)	0.022	1.79	0.303	0.099
24.	Nitric acid, concentrated	4.272	0.069	1.61	0.276	0.090
25.	Nitric acid, concentrated	4.299	0.066	1.54	0.264	0.086

Plate B (size of samples, 2 by 2 inches; 5.08 by 5.08 cm.).

26.	Lead acetate and sodium hydroxide	5.202	0.064	1.23	0.248	0.081
27.	Lead acetate and sodium hydroxide	5.314	0.066	1.24	0.256	0.084
28.	Lead nitrate and sodium hydroxide	5.341	0.066	1.24	0.256	0.084
29.	Lead nitrate and sodium hydroxide	5.420	0.071	1.31	0.275	0.090
30.	Lead chromate and sodium hydroxide	5.526	0.063	1.14	0.244	0.080
31.	Lead chromate and sodium hydroxide	5.452	0.065	1.19	0.252	0.083
32.	Aluminium nitrate and sodium hydroxide	5.374	0.071	1.32	0.275	0.090

(a) Size of sample, 1.45 by 5 cm.

Standards for Tin Plate.

The quality of a galvanised iron is determined chiefly by the thickness of the coating, since zinc, under ordinary service conditions, itself corrodes and inhibits the corrosion of iron even after the latter is exposed. Tin, on the other hand, frequently accelerates the corrosion of iron; its protective influence is mechanical. Uniformity of coating is therefore an essential requirement for good tin plate, and a test, such as the one devised by W. H. Walker (*Journ. Ind. and Eng. Chem.*, 1909, i., 440), for the detection of pinholes and other inequalities in tin plate is of great importance in determining quality. Leaving out of consideration the question of the purity of tin plate, it is evident that specifications should require certain standards, both for thickness and for uniformity of coating.

Obviously the amount of coating necessary for good tin plate will depend, to a large extent, on the service to which it is subjected. The specifications for the United States Navy Department (No. 47 T 1, February 15, 1912) call for 5 pounds of tin per 112 sheets 14 by 20 inches in size, corresponding to a coating of 1.123 grms. per square decimetre (0.367 ounce per square foot). According to Serger (*loc. cit.*), a coating of 0.3 gm. of tin per square decimetre of tin plate (that is, 0.15 gm. per square decimetre of surface) is sufficient to make plate resistant to the corrosive influences to which canned goods are subjected, and no material which had given satisfactory service showed a smaller amount of tin. The few data at hand in the Bureau of Science tend to confirm the conclusion of Serger, and indicate that the figures given by him represent the lower limit for good tin plate. For example, a certain shipment of tin cans corroded so badly during an eighty-day voyage from the United States to Manila that a large amount of the contents leaked out. The corrosion was entirely from the outside, the interior of the cans remaining bright and unspotted. There was no evidence of sea-water damage or undue corrosive influence. Upon analysis the cans were found to have a coating of 0.245 to 0.250 gm. of tin per square decimetre.

Summary.

A number of methods of stripping tin plate without attack on the iron base have been studied. Of these, detinning by means of an electric current, making the plate the anode in a bath of sodium nitrate, and stripping by immersion in a solution of a lead salt made alkaline with sodium hydroxide (sodium plumbite) can be recommended for rapid and accurate analytical work.—*The Philippine Journal of Science*, xi., Section A, No. 4.

THE CO-EXISTENCE OF MATTER AND ENERGY.

By FRANCIS A. DUGAN.

(Continued from p. 239).

If matter in the liquid state acquires a greater velocity its cohesion should be less. Our liquid portion supports this statement. The higher the temperature and similarly the greater the velocity and the less the cohesion. Our molten material, as it become more highly heated, is very mobile. It reaches a point where its cohesion is so little, relatively speaking, that it rises by capillarity in the wick, and burns, giving us the gaseous state of matter.

We can make some observations on gaseous matter, but before doing so I might mention that in this state, whether the matter is free by itself or combined with some element of the atmosphere, need not to be taken into consideration for the point I wish to raise. It is in the gaseous state and possesses the same physical properties that it would possess if not combined with some element of the atmosphere.

Let us examine our gaseous matter. Where is our property of cohesion? It has apparently disappeared, and our matter seems to possess now a property directly opposite, its tendency is to diffuse. I do not wish to infer that cohesion has entirely vanished. It has not, and I cannot conceive of matter wholly losing any of its attributes. I believe that a property possessed by matter in any one state must be possessed by it to a greater or lesser degree in any other state in which it is capable of existing, and I believe these states are many.

Here we may draw one conclusion, and it is this, that the property of cohesion possessed by matter is dependent on motion for its existence.

We can attribute one property of matter to velocity. Cohesion and velocity are functions of each other, and if this is true, we might be able to make a similar statement in regard to all other properties of matter if we knew the motion of our elements.

In the gaseous state of matter our molecules are in a very rapid state of motion. We can best see the results of this motion by beginning our observations with the solid state of matter.

Solid matter, as we know, is capable of standing free and superimposed, while for our liquid state it is necessary to furnish a retainer; an open vessel is satisfactory, but when we endeavour to restrain the gaseous state we find

that an open vessel is not equal to the task and it is necessary for us to use a sealed one. It should also be noted that not all so-called solids will be suitable for the purpose. Our vessel must be of a certain class of solids, that which is of an impervious nature, otherwise our gas will escape through its pores, and it should also be remembered that the lighter the gas the greater is its translatory velocity and therefore the more difficult it is to restrain it.

Aside from the fact that a sealed vessel is necessary to restrain this state of matter, we know that the gas itself exerts a pressure upon the vessel. The motion in this state of matter is such that it possesses marked kinetic energy.

We can observe from our three states of matter, that the more dilute the matter the greater is its tendency to move, or the greater is the manifestation or revelation of energy.

Matter in passing from the solid to the liquid state underwent a great change. It, however, undergoes a far greater change in passing from the liquid to the gaseous.

If there existed a state of matter more dilute than a gas I believe we could safely say, judging from the progressive properties of matter as we know them, that the change effected in passing from the gaseous to a more tenuous state would be far greater than any change that had preceded it and it, might even be possible, at first, to overlook the fact that matter could be capable of existing in such a form or be capable of possessing such properties.

If we assume matter as being capable of existing in a state more dilute than a gas, what properties could we reasonably attribute to such a form of matter?

In the first place we must admit that such a state would be a very attenuated form of matter and its motion must be incredibly rapid.

If this is so one might think that it would be impossible to restrain this form of matter, even in a sealed vessel, as we did a gas. Viewed from the progressive order of matter it should be capable of readily penetrating all solids.

We might infer that this state of matter, due to its high velocity, would be noticeably energetic, much more so than a gas, and if it was capable of penetrating all solids readily, as it certainly would be if such a state existed, it would reveal its energy to us, if such was at all apparent, in some peculiar manner.

We might also think that in passing from the gaseous to this tenuous state that matter might, apparently, lose some very important attribute, as we have noticed how cohesion has apparently vanished in passing into the gaseous state.

Matter in passing into such a state, as here assumed, could apparently lose many of its attributes and still be consistent with what we should expect of such a state of matter. It could also apparently gain some new properties or possess them to a higher degree than a denser state of matter and also be consistent with what we should expect; in fact it should possess to a higher degree some properties attributable to matter with which we are familiar, such as, for instance, the property of elasticity.

Perhaps the assumption of a state of matter more dilute than a gas would be of less interest to us if we were not familiar with manifestations of energy in such a medium. We are, however, familiar with such manifestations and we know what relation they bear to mass in motion.

I refer particularly to heat, but light being of a similar nature must likewise be included.

In the flame of our candle we can observe that we have a point where a great change is being wrought. Matter is changing in a noticeable measure into one of two things. It is passing into a something of which we have not the slightest understanding, that which we designate as energy, or forms or species of energy, light and heat, a something not material but which, under some unknown conditions, can assume a material form. If this is not correct then matter is passing into a state more tenuous than a gas and

in doing so is affecting a form of matter, common to itself, in a vibratory manner.

We must say one or the other, either matter is changing its state or there is no such thing as actual matter.

I believe that in the flame of the candle matter is changing through the gaseous to a more tenuous state, and we have present, as agents, light and heat.

What is light or what is heat? We say they are forms of radiant energy. Of course this is true, as they are energetic, but this does not tell us much. We say they are vibrations in the ether, but as we do not know the composition of the ether we are still unable to grasp an understanding of them.

To understand them we should know the composition of the ether. We are therefore confronted with the old question, Of what is the ether composed?

I look upon this question as one for the chemist to answer, and if he is to answer he must view the ether from a chemical standpoint only.

The chemist views and explains the composition of any substance from a chemical standpoint, it would be absurd for him to do otherwise; still the ether is the one thing of which he makes an exception. Why make an exception in this case? There is no valid reason for doing so.

If we are to look upon the ether from a chemical viewpoint, or from a natural viewpoint, which is equivalent to the same thing, then we are forced to admit that the ether must be composed of chemical matter. This must be admitted. Nothing else can exist.

Viewing it in this way we already have an inkling as to its composition, and we must say that it is different from any matter with which we are familiar. Can we say that it is composed of some unknown element? No, such a view would not be in harmony with things chemical. Then it must be matter existing in a form more dilute than a gas. This deduction is not unreasonable; in fact, it seems to be the only logical answer at the present time.

I therefore believe that the ether is material in nature and possesses mass. When I say that light and heat are vibrations in the ether I mean that they are just as material in nature as sound, and, like sound, are propagated by mass in motion.

I believe we have ample proof at hand that such is the case. If light is in mass in motion or manifestations of mass in motion, then it should, in all respects, conform to the laws of moving bodies. This it does.

It travels in a straight line. We know that all mass in motion exhibits this tendency. It also travels more easily through a lighter medium than through a denser one; that is we can, in a measure, obstruct its passage by interposing a medium of some suitable material. It can be reflected, and on reflection the angle of reflection is equal to the angle of incidence. This is but the law of reflected motion, and all mass in motion obeys this law. The more elastic the body the more apparent the reflection. From the property of reflection alone I believe we can safely infer that light must be very elastic or that it is a vibration in a medium wonderfully elastic. We know the ether to be a perfectly elastic medium; it possesses in the highest degree a property which is common to matter and this property alone should tend to identify it as matter.

If light, or the medium in which it vibrates, does not possess mass, what explanation have we to offer for such phenomenon as refraction? We have none. If on the other hand the ether does possess mass then our phenomenon of refraction is readily explainable.

We know that light on refraction, or when it passes at an oblique angle from a rarer to a denser medium, is bent towards the line of the perpendicular.

Let me assume that I have a disc of some material and that it is possible for me to project it in any given direction at will, and at the same time impart to it sufficient motion to carry it to any predetermined point. Such an object will serve to represent the cross sectional construction of a ray of light.

I will now project the disc, at an oblique angle, towards the surface of a pond of water and we will notice what happens at the point of contact. The lower end of the disc coming first in contact with the water, which is a denser medium than the air, will be retarded, while the upper portion, still in contact with the rarer medium, is free to continue to travel; the result is that the line of motion will be changed, the disc being bent towards the line of the perpendicular, and if sufficient motion had been imparted the disc would travel through the water at a different angle from that at which it struck.

Light, we know, behaves in the same manner, and we have, on refraction, a similarity to mass in motion.

If I had projected the disc from the perpendicular it would travel through the water perpendicularly, as all portions of the disc would pass from the rarer to the denser medium at the same time.

If the direction of motion be reversed and the disc be projected from the water to the air the opposite of this will hold true.

Light, as we know, acts in the same manner. Why have we these similarities of light to mass in motion? Why do we neglect to endeavour to connect them? If we do not connect them then we must view them as coincidences or as accidental relations in the make up of natural science.

In the regions of so-called space we have examples of matter assembling, or as it is said, forming, which are termed nebulae. The Nebula of Orion is thought to be forming from the constellation itself, although both are separated by a great astronomical distance; still the elementary character of each is similar, which gives credence to this supposition.

Whether the Nebulae is forming from the Constellation or whether it is entirely independent of it, the fact remains that it is forming and it is coming from somewhere. Matter, therefore, must be capable of assuming some state which carries with it migratory properties.

Matter in the gaseous state does not possess such a property—it must be a much rarer state of matter, and in this state whether or not it possesses elementary character is immaterial, such a state of matter; from the very nature of things, must exist.

We turn our attention again to the candle and grant that it is now completely and perfectly consumed; during its consumption, however, we have had a great display of energy, some of it undoubtedly coming from the atmosphere, but some of the energy must have emanated from the candle. We have seen the candle change from the solid to the liquid state and through the liquid to the gaseous state and it now exists as gaseous matter plus some light and heat.

In the gaseous state matter has a very rapid motion, much more so than the solid or liquid, and in the gaseous state matter is more dilute.

If we except the quantity of what we term energy added or absorbed to effect the change of state then we can have no more energy present in one state than in another, but still their motions are vastly different. How then can we harmonise matter with this change of motion? To me it is evident that the mass must be correspondingly less to equalise the energy, the energy must be equal if we had comparable conditions. My conclusion is that matter must move with equal energy. We have proof of this order of motion of matter in the gaseous state. At any given temperature the translatory energy of all gases are equal.

The rate of effusion of hydrogen to oxygen is as 4 : 1—here there is a relation to the square roots of their densities and their rate of diffusion is the same. We are able to determine the atomic weight of a gas by means of its rate of diffusion. Matter in this state must have a motion which bears a definite relation to its mass, and the relation is mass times velocity squared.

The Law of Avogadro states—"Under the same temperature and pressure equal volumes of all gases contain

the same number of molecules." Considering this law we could also state that under the same temperature equal volumes of all gases containing the same number of molecules exert an equal pressure, or that at the same temperature an equal number of molecules of all gases exert an equal pressure, or further, without changing the law one iota, we might state that at the same temperature molecules of matter in the gaseous state move with equal energy.

If the energy of all gases is equal at any given temperature, where comparison can be made, why is it not equal at different temperatures? I believe we will know this when we look upon heat other than from a standpoint purely of energy.

If matter in the gaseous state is moving with equal energy, why is matter in other states not doing likewise? We admit that all matter is in some sort of motion. If so, what is its motion? I believe it would be a very peculiar and irregular condition if solid or liquid matter possessed a motion which bore no relation to its mass, and then to assume this relation in the gaseous state.

This line of reasoning would lead us to believe that the molecules of solid or liquid matter must have a motion that bears some relation to its mass; therefore one would naturally infer that the relation was the same as that of gaseous matter, and we would be justified in our inference, as we have evidence of matter in states other than gaseous conforming strictly to this rule.

Van't Hoff has shown that in a solution of a non-electrolyte, such as a solution of sugar in water, the concentration was proportional to the osmotic pressure. It obeyed Boyle's law for gases. He showed, further, that the osmotic pressure increased with the temperature, obeying Gay-Lussac's law for gases, and finally the law of Avogadro was strictly applicable, because, in a solution of equal concentration of matter, the osmotic pressure was equal to gas pressure.

Sugar crystallises and is admittedly a solid, and when in solution in equal, and therefore comparable, quantities with gases, it exerts an equal pressure; there is no thermal change when sugar is dissolved in water, no energy is set free and none is absorbed, as it is a non-electrolyte; therefore, it must have possessed in the solid state the energy it displays when in solution.

This, I believe, tells us without a doubt that at least a certain class of solids, when brought into solution, possesses this order of motion of equal energy. The osmotic pressure of electrolytes does not obey Avogadro's law, the pressure of such being higher. This is not a condemning, but is rather a supporting circumstance; they should show a difference, as we know that they go into solution differently.

Jones and his co-workers have done much to establish the solvate theory, and have proven beyond a doubt that such salts combine with a portion of the solvent, and this evidence is put forth, at the present time, to account for the greater osmotic pressure of such salts.

Le Blanc has shown that in the electrolysis of normal solutions of strong acids which, as is known, contain the same hydrogen ion equivalent that their ionic decomposition value is equal. This is what we should expect. It is also shown that the ionic decomposition values of normal solutions of bases were also equal. This we should also expect; but we have no right or reason to expect that the same figure is identical for both. This tends to show that the hydrogen and hydroxyl ion possess the same energy.

In this line of experiment the ionic decomposition value of salts was found to be greater than acids or bases, but if such salts enter into combination with a part of the solvent and absorb heat on solution, we measure more than the decomposition value of the salt and the figure should be greater. It is a parallel case with the osmotic pressure of such salts.

Our law of inertia tells us that a body once set in motion

will move for ever in a straight line unless it is acted upon by some external force.

The mere observation of such a law I consider as evidence that motion is a common property of all matter, that matter is already in motion and the mere imparting or stopping of motion is only apparent. We can change the place of objects, but we cannot impart to them any more motion or energy than they naturally possess.

If we could actually stop the motion of a moving body by meeting it with equal energy or by acting upon it with some external force, as in the catching of a baseball, there would not only be a loss of energy from the moving ball, but there would be a similar or equal loss from the energy expended in stopping it.

We know the energy of a moving ball, if suddenly stopped, to be manifest as heat, but, in this respect, we say the species or form of energy changes.

It is wonderful how small a quantity of matter travelling at the velocity of heat would possess what we would consider tremendous energy. A trolley car, weighing 12 tons and moving at the rate of 10 miles an hour, which is high speed for city transit, is considered a very energetic object, but it would take less than 0.000003 of a milligram of actual matter moving at the velocity of heat to equal it in energy. We know the energy possessed by the car must be at least equal to that supplied in the electrical form, and similarly as with heat it would take an insignificant quantity of matter in the electrical form to equal the energy of the car.

To set a body in motion, energy must be applied, and the energy must cause a change in the mass of the body before motion is imparted. When a body is in motion, it must expend its energy before it can be stopped, and this expenditure must cause a reverting change in the mass before the body is stopped.

I believe it is due to this change of mass that we owe our property of inertia.

Time is a factor in everything, even in all chemical operations. This consideration alone, I think, would tend strongly to support the arguments I raise in this paper.

If, when put in motion, the mass of a body did not change, then communication of motion should be instantaneous, and if a body was in motion it should be possible to stop it instantaneously by a counteracting force. It should possess no inertia. We cannot impart to matter any property other than that which it already possesses.

We can, by what we term physical means, apparently impart to matter new properties, such as tempering steel, hammering or rolling brass, &c., but neither of these are physical changes, as they both necessitate a change in the mass; we have added no new properties to the matter, we have merely intensified properties which are common to all matter, and we accomplished this by changing the matter. As I view it, matter cannot be changed in the least, without a change in the mass and the motion, and we can impart to matter no new property.

If motion was not a common property of matter, I believe it would be an impossibility to move a single object.

We cannot, as the law of inertia would lead us to believe, say that rest is a property of matter or a condition matter is capable of possessing, as rest is an unknown condition, and is to be found nowhere in the universe. We have not the slightest proof of any matter being dormant.

I cannot consider the electron as the ultimate unit of matter, as I believe it capable of existing as the medium in which heat vibrates, and this medium must possess mass and, therefore, consist of units of matter more dilute or attenuated than the electron. I cannot see how there could be such a thing as an ultimate unit of matter. Regardless of how small the unit or how dilute the mass it must be susceptible of divisibility. Indivisibility is an inconceivable condition, matter must extend in dilution to the infinite.

Our elements must differ from one another by more than

a different numerical grouping of electrons contained in the atom, because if this was the only difference in their atom they would be all alike, excepting in the respect of that of density or magnitude, and any one chemical reaction would be applicable to them all, time being the only different factor in reaction.

I believe we have no right at all, or in fact no proof that would warrant us in saying that the atom of any element is composed of electrons. It is true there has been obtained from the atoms of different gases, both elementary and compound, a like unit of matter which is termed the electron, but I do not consider this sufficient to warrant us in saying that this electron existed in the atom in that form. It would be just as logical to say that the heat derived from the combustion of the candle existed as heat in the atom of the candle and the oxygen of the air.

I doubt very much if anyone would make this assertion, even if heat or its medium had been found to possess mass; still it would be just as reasonable to make such a statement as it is to make the statement we do in reference to the electron.

We may assume the atoms of all elements to be composed of a like unit of matter, and we may, if we wish, call this unit an electron, it matters not what we call it.

If we assume that these electrons are in motion and that their velocities differ in different elements, then we can at least have an understanding of why differences should exist in our elements. A like unit of matter moving at different velocities affects our senses in markedly different manners, and it is this that makes me believe that the atoms of our elements differ more in velocity than they do in any numerical grouping of electrons.

By assuming that all elementary difference is that of velocity, we can understand why such a thing as periodicity should occur in the elements. Lithium, Sodium, and Potassium are good examples in progressive order; they vary, one to the other, by an octave.

In music we know one note is an octave above another when its vibrations are doubled, and I believe it is proper to look upon potassium and sodium in a similar manner.

There are octaves among our elements, octaves in sound, and octaves in odours, and I believe there is a relationship in their velocities; in fact, I believe that ultimately it will be found that there is more harmony in Chemistry than we at present conceive; that is, any chemical compound which is pleasing to the sense of smell, is, or would be, pleasing to the sense of hearing if by any means it were possible to render audible its vibrations. On the other hand discord would be produced if it were possible to render audible the motion of some of the sulphides, the effect upon the sense of hearing would be repulsive.

To-day we look upon all chemical reaction as of an electrical nature. The Ionisation Theory presents this view of matter to us. I do not wish to find fault with this theory; I do wish, however, to know the cause of ionisation, or to get at the basis of all chemical action. One cannot, however, understand it unless he views it as one of motion. I therefore look upon all chemical reaction as based primarily on motion, that is, a relation of mass to velocity, or more strictly speaking, to a difference of intensity of energy between two reacting substances.

Intensity of energy can accomplish that which its mere equivalent cannot. This could be observed from the candle. Heat alone will light it, but its mere equivalent, in another form, would deform it.

If we will consider this fact thoroughly, I believe we will ultimately reach the conclusion that a difference of intensity of energy between two reacting substances must be taken into consideration and studied if we ever expect to find the prime cause of chemical reaction.

If all matter is, as I assume, in motion, and moving with equal energy, hydrogen—which is matter in its most dilute form, as we know it at present—should therefore possess the greatest velocity. We know this to be the case in any unit of this form of matter.

In the gaseous state its molecule moves with a greater

velocity than does that of any other gas, and in the ionic condition the H ion moves by far the fastest of all ions.

If chemical reaction was based on motion, or intensity of energy, hydrogen should be the most chemically active element known. In reference to its deportment in compounds it is, beyond question, the most chemically active element we have.

The magnitude of its activity will be forcibly impressed on us if we will but eliminate it from our elements. Do this and you will annihilate chemistry, as hydrogen, I judge, enters into at least 85 per cent of all chemical reactions; whether the hydrogen is in an acid and being replaced by a metal, or whether it is in some compound which is not an acid and being replaced by some other element or radical, the hydrogen readily enters into the reaction.

In the formation of water it is written as an afterthought, that is at the end, of most chemical equations. It is, in general, of such frequent occurrence that we pass but little comment upon it, and most naturally insert it as it really is formed, and it balances the equation.

It occurs too often not to have some significance; in fact, I look upon the formation of water as the prime cause of the reaction, as it is the disturbing influence of hydrogen that brought it about and rendered the reaction possible.

We have, in natural science, a great many laws for various phenomena, expressing variation as the square root of some numeral, or as the square of some numeral. These are too numerous not to be related. I think they are not only related, but are telling us the same thing in different ways, or they are the natural consequence of some one law.

We have the same identical law for what we consider different phenomena; for example: The laws of reflection of light, heat, sound, and any moving mass are the same. Our three laws for gases are applicable to osmotic pressure. The laws governing the intensity of light, heat, sound, gravitation, and any mass in motion are the same.

We know this to be so, but we do not try to connect them. Why? We look upon their similarity as an accident or as a coincidence. In this respect I believe we are wrong.

We have to know all things by similarity, and if one thing is exactly similar to another we call it the same thing, but when we turn our attention to the field of science we make an exception to this rule, as we deem it incredible that different phenomena could be a like manifestation of the same thing.

We do not endeavour to connect light, heat, and sound. We think them different because sound is a wave motion in a medium with which we are familiar, while light is a wave motion in a medium which we do not understand. We think them different also because a light wave possesses a motion which is transverse in all directions, but it is undeniable that it travels forward with a velocity so much greater than sound that it may be said to be incomparable.

In a sound wave there cannot be a condensation without a transverse motion. This became apparent to Mayer in his calculation of the mechanical equivalent of heat, as determined by the velocity of sound, obtaining a figure exactly the same as that given by Joule, and it was Mayer's method of taking into consideration the pressure of the atmosphere, or the lifting of the atmosphere, which proves a transverse motion, that enabled him to make such a calculation.

It is this similarity, and many other apparently manifest similarities, in other fields, that makes me positive in my statement that, if any two things, phenomena or whatever else it may be, resemble each other, it matters not in what respect, the reasons for such similarity are as closely related as is their condition of similarity, or I might state it differently: There is no such thing as a coincidence or an accident in relationship in the entire makeup of Nature.

THE DECIMAL SYSTEM.*

By HARRY ALLCOCK.

THE lecturer urged that the interests of the State, of Capital, and of Labour, make it vitally necessary for us, even now in the midst of war, to take stock of our position in regard to the selling side of our export trade, and to adopt such agreed improvements as will be likely to enhance our prospects in that direction. In the past we as a nation have possibly been too prone to hold the view that as we were in effect the sole workshop of the world, it was a matter of indifference to us that our customers abroad should be confused and irritated by our complicated business systems; but to-day we have to admit that other nations are challenging our manufacturing supremacy, and that they have succeeded at least so far as to provide alternative sources of supply for those of our customers who were formerly obliged to come to us for their requirements, notwithstanding our discouraging methods. Other things being equal international trade naturally flows along the lines of least resistance, and it is accordingly necessary for us to describe our goods in the language of the countries for which they are intended, and otherwise so to improve our business systems as to make it easy for our present and potential overseas customers to trade with us. Every commercial contract contains references to money, weights, or measures, and frequently to all three, and it follows that the simpler and more widely understood are the bases of these three fundamentals, the better for those negotiating such contracts. As our national existence depends on our ability to sell manufactured goods to all nations, that is to develop a world-wide trade, the United Kingdom would benefit more than any other nation by the establishment of the universal systems of currency, weights, and measures.

Coinage.

In view of the diversity of the units of value employed by different countries it is clear that a world-wide universal system of coinage is unattainable at the present time. But apart from countries forming parts of the British Empire, practically all countries of the world employ a decimal system of coinage, and it is also noteworthy that the British Empire is not solid in abstaining from the decimal basis, since Canada, Newfoundland, Egypt, the Straits Settlements and adjacent possessions, Ceylon, British East Africa, and Uganda, and many other of our smaller possessions have decimal coinage. Since all financial transactions involving such everyday matters as dividends, discounts, and commissions are paid on a rate per cent—i.e., per 100, not per 20 or per 240—adoption of a decimal system of coinage would result in substantial economies of both time and labour.

In giving effect to the demand for the decimalisation of our coinage, the object should be to retain as much as possible of the existing system, in order to reduce to a minimum such inconveniences as are incidental to any change. The desirability of retaining the sovereign if possible is generally admitted. Fortunately the present florin is the exact tenth of a sovereign, and if it were divided into 100 cents or mils instead of 96 farthings the decimal chain would be complete.

Weights and Measures.

As regards a universal system of coinage external influences such as fluctuations in the rate of exchange would always prevent international coins of equal nominal value from having always the same actual value. But such extraneous influences do not affect weights and measures. The growth in the adoption of the metric system, which is now obligatory in 34 countries with a population of 437,330,000, and optional in 11 countries with 727,233,000, goes to prove that the choice of such a

* A Lecture delivered at the Institution of Civil Engineers, Mar. 27 1917.

universal language is now limited in effect to the British Imperial System, and the International Metric System, which is a scientific system having advantages demonstrated by the decimal relation between the units, the extremely simple relation of the units of length, area, volume, and weight to one another, and the uniform and self-defining names of the units.

In 1897 the use of metric weights and measures in Great Britain was permitted by law, and a favourite argument against making the metric system compulsory is that by merely prolonging its permissive use side by side with the existing British system the better system will ultimately survive. A similar argument is that those desiring the metric system should lead the way by conducting their business solely on that system; but such voluntary piecemeal adoption cannot be expected, because the pioneers would thereby penalise themselves by being thrown out of touch with their neighbours.

Attitude of Engineers.

In the course of the debate in the House of Commons in 1907 on Lord Belhaven's Metric Bill, which was rejected by the small majority of 32, though it had passed the House of Lords in 1904, Mr. Haworth stated that 80 to 90 per cent of engineers were opposed to the metric system. The lecturer said that he did not know whether that statement was correct or not at the time, but it would certainly not represent the views of our engineering firms now. In 1915 a special canvas showed that firms engaged in the electrical and allied trades were in its favour in the proportion of four to one. Of the replies received to a questionnaire issued to all the members of the British Engineers' Association in January last, 90 per cent, 87 per cent, 86 per cent, and 83 per cent respectively were in favour of the adoption of decimal coinage, metric weights, metric dry and liquid measures, and metric linear measures. Of 3026 replies received by the Decimal Association recently in answer to inquiries addressed to 25,000 British firms of a widely diversified character, 2994 were in favour of decimal coinage and metric weights and measures in the United Kingdom.

Some British manufacturers fear that on the day a Metric Act becomes law they would have to scrap all their existing patterns, tools, and other workshop standards; but in the draft Metric Bill now being prepared by the Association of Chambers of Commerce, and aiming at making the metric system compulsory in all commercial transactions, there is a clause providing that nothing in the Act shall affect the manufacture and use of any machinery, tool, or other article made by other than metric measures. Hence, manufacturers would be at liberty to continue the use of the existing weights and measures for manufacturing purposes until they chose to amend them.

Engineering Workshop Practice.

As regards the effect of the introduction of metric weights and measures on engineering workshop practice, the lecturer relied for the expression of his views on a long quotation from an article in the *Electrical Review*. In this it was stated that so far as concerns existing drawings and designs no changes in dimensions would be necessary, and only their names must be altered. Measurements usually stated in thousandths of an inch could be expressed in hundredths of a mm. to a closer degree of approximation than could be worked to in the shops. For very fine work, necessitating in English units measurement to the fourth place of decimals, the hundredth of a mm. served all ordinary purposes, giving a maximum departure from true equivalence of 0.0002 in. The operator working to gauges, jigs, and templates had nothing to do with the figured dimensions, and therefore no trouble could arise from the use of the metric system on drawings; those who had to take measurements direct from drawings were *ipso facto* shown to possess a reasonable degree of intelligence, and therefore readily became accustomed to the use of the new units. With regard to standards, such as those of the

Engineering Standards Committee, it was a mistake to suppose that, as Dr. C. C. Garrard had suggested in *The Times Engineering Supplement*, they would all have to be scrapped. They need not be altered at all, though as they came under revision they could be modified if it were desirable. Steel rails, for example, could be sold as easily by the metre or metric ton as by the yard or ton, and in course of time, on the re-issue of the specifications, the dimensions of the flanges, treads, &c., could be re-figured in mm. Again, many standards were merely nominal, and might just as well be denoted by letters or numbers as by figured dimensions, as the latter were not used in practice. No difficulty need be anticipated in adapting many of the standard specifications to the metric system, with practically no breach of continuity or inconvenience to manufacturers or users of the materials. But there was undoubtedly a difficulty in connection with rolled and drawn metal sections, such as rods and bars and shafting, of which during the transitional period it might be necessary to carry stocks in both dimensions; these, as well as drills, would eventually have to be provided to even metric sizes, but in very few other cases would even measures be necessary.

The lecturer also pointed to the advantages of using the metric system as the basis of designs, because the scientific men of the world have already established that system as the basis of their calculations and experiments, and he referred to the belief once expressed by Lord Kelvin that at least half of the work of clerks and draughtsmen in engineers' and surveyors' offices is entailed on them by the present farrago of weights and measures. He thought it probable that the reorganisation of our workshops for the production of new plant of all kinds after their concentration on munitions manufacture will involve many new designs, tools, and processes, and suggested that this approaching time of flux will provide an excellent opportunity for all to start afresh on the metric basis.

JAPAN'S CHEMICAL INDUSTRIES.

ONE of the most remarkable features of the economic development of Japan is her extraordinary progress in the chemical industry. At the commencement of the war this industry was still in its infancy, yet to-day Japan is exporting chemical products for the supply of which she was but three years ago almost entirely dependent upon outside sources. The question arises whether, when the conditions which have contributed to her progress have been removed, Japan will have secured the foundations of this new industry sufficiently well to maintain it. Without an adequately protective tariff it is doubtful whether she will, for in spite of the availability of some of the raw materials in Japan itself or in countries near at hand, in spite of the great advantage she possesses in cheap labour, and in spite of the access Japan enjoys to cheap motive force by reason of her abundance of waterfalls, the chemical industries of Europe and the United States have gained such a footing in all parts of the world that a new competitor is bound to have a very hard fight for existence when times are normal again. Nevertheless, realising as we do the power of Japan's industriousness and her genius, we can anticipate the time when Japan will take her place among the chemical-producing nations. But such time may be delayed a little longer, for it must be remembered that the chemical industry in Japan is by way of being an emergency industry. Unable to obtain adequate supplies of chemicals from the ordinary sources of peace time she has produced her own, and in some cases produced sufficient for export purposes. For the most part, however, Japan's chemical factories, so we are informed by a Japanese authority who has recently arrived in this country, are sufficient only for small-scale production; the capital invested is not large, so that if it is found after the war that the industry will

not resist competition, some of its branches can be discarded with the minimum of loss.

It may seem a strange thing to say, but the chemical manufacturers of this country can regard without envy the advent of Japan as a new competitor. It is Germany that stands to be the largest loser through the development of the Japanese dyestuffs industry. For many years to come Japan is bound to be a large customer of Great Britain for soda-ash and caustic soda; in fact, as she develops her other industries her need for these alkalis will become greater and greater, and lacking what we possess, abundant supplies of cheap salt, it is at least doubtful whether Japan will be able in the near future to produce sufficient alkali to satisfy her home requirements. The production of soda was started in Tokyo, Osaka, and Yamaguchi Prefectures some thirty years ago, but owing to the comparatively high cost of salt, development has been slow. At the present time soda is being produced by an old system by the Kanto Sanso Kaisha of Tokyo Prefecture and the Onoda works of Yamaguchi Prefecture. According to Dr. Toyokichi Tamatsu, one of Japan's distinguished industrial chemists, means have been studied for supplying industrial salt at a lower cost, and, in addition, for working the ammonia and electro system of soda making. But we doubt whether the view expressed in some quarters in Japan that the home demand will be met entirely with the domestic products in the near future is not too optimistic. Those engaged in Japan's progressive soap and glass industries—to mention only two of the commercial uses of alkali—would hardly consent without protest to a heavy protective duty on soda-ash and caustic soda.

Turning to another branch of the chemical industry, Japan has made wonderful progress in the production of phosphorus; before the war, Japan imported all the phosphorus she required for her match industry from England, France, and Germany. But now the Chemical Industry Company and the Fuji Electric Chemical Company are manufacturing phosphorus from phosphorite imported from the Southern Pacific Islands, and some idea of the size of the output can be obtained from her huge export trade in matches. During 1915-16 (as stated in *The British Trade Review*, November, 1916, p. 222) she exported 15½ million gross of matches to India alone—this in spite of an Indian Customs duty of 7½ per cent. Whether, when English phosphorus again becomes available for export and prices become normal, Japanese phosphorus will be the cheapest product for the match makers to use remains to be seen. But judging from the price at which Japan has been able to sell to India matches made from Japanese phosphorus, it would seem that the cost of its production from phosphorite is relatively low. Another match-making chemical, potassium chloride, is being produced on an extensive scale in Japan, at Aidzu, where the water power at Lake Inawashiro is utilised, and at various other places. It is also estimated that 10,000 tons can be made annually from seaweeds gathered on the coasts of Hokkaido, Karafuto, Chiba, and Kanagawa districts. Japan is also making sulphate of ammonia from by-products of the gas and coke factories and from nitrogenous lime. The production of acetate of lime by the Japan Acetic Acid Company has also increased, and it seems probable that America will lose a good customer for the acetate. The Tokyo Gas Company is making carbolic acid, and the Japan Dyestuff Company has laid plans for manufacturing it from benzol. The yearly production of sulphuric acid in Japan is little short of 750,000 tons, and it is intended to establish plant for the production of this acid by the contact process. As to the dyestuffs industry, it is common knowledge that the Japan Dyestuffs Manufacturing Company has been founded, and is backed by the Government. Before the war Japan imported from Germany coal-tar colours to the value of something approaching £1,000,000, and, although the Japanese industry is still in its infancy, it is quite clear that Japan does not intend to go on paying such a tribute to Germany.—*The British Trade Review*, May, 1917.

THE PATHOLOGY OF VENEREAL DISEASE.*

By F. W. MOTT, M.D., LL.D., F.R.S.; Major R.A.M.C. (T.).
Consulting Physician, Charing Cross Hospital; Pathologist
to the L.C.C. Asylums; late Member of the Royal
Commission on Venereal Diseases.

THE lecturer stated:—The first duty of the State is to prevent disease, failing that to cure disease, and failing that to prolong life and relieve suffering. This dictum, he believed, would especially commend itself to a meeting held in the Royal Institute of Public Health, and particularly at the present time, when the influence of venereal infection upon the health of our manhood and the birth of healthy children is of the greatest national importance.

Huge sums of money have been expended in the past in the building and upkeep of costly infirmaries, lunatic asylums, and homes for the blind, the deaf, the paralysed, and the feeble-minded, and it had been shown by the evidence given before the Royal Commission that a considerable portion of the population in these institutions would never have been in them had it not been for venereal infection.

The Government, by adopting the recommendations of the Royal Commission to establish centres for diagnosis and treatment, and Parliament by granting, in 1914-15, a sum of £50,000 per annum for laboratory facilities, with a view to the prevention, diagnosis, and treatment of diseases in general, have at last awakened to the value of pathological research. *Fiat lux* should be the remedy for the hidden plague.

Pathology has done its work; it has found the cause and how it can be remedied by showing that venereal diseases are due to infection by specific micro-organisms, which, after entering the body, at first multiply at the site of inoculation, producing a characteristic inflammation; they then spread to other organs and tissues and give rise to constitutional disease which is difficult to cure. The obvious course is to prevent the organisms entering the body by adopting suitable prophylactic measures; failing this, to diagnose the existence of the specific organism while it is still producing only a local reaction and employment of modern curative treatment with a view to destroying the organisms before they can generalise and colonise in the organs and tissues of the body. The adoption of preventive and curative measures will be a great economic saving by preventing a number of chronic, incapacitating, and fatal diseases.

The lecture was illustrated by a lantern demonstration of numerous photo-micrographs of the specific organisms and the microscopic structural changes they produce in the organs and tissues of the body.

HISTORIC COAL-TAR PRODUCT.

PREMIER ANTISEPTIC FOR WOUNDS DISCOVERED BY
BRITISH DOCTORS.

A CORRESPONDENT sends the following communication:—

One of the most interesting of the coal-tar products has been discovered during the last year of the war by British doctors. It is the most efficient antiseptic that has yet come to light, and, by an irony, is covered by a patent for a German acridine dye!

Before the Controller (Mr. Temple Franks), in the Patents Court, on Friday, Messrs. Blandy Bros. and Co., of 11 Mark Lane, London; Messrs. Levenstein, Ltd., of Manchester; Messrs. May and Baker, Ltd., of Battersea; and Boots Drug Co., all applied for licence to manufacture under Patent 24652 of 1910, in the name of Leopold Cassella and Co., of Frankfurt-on-Main, a substance to which applies the trade-mark TRYPA-FLAVIN. The patent

* Abstract of lecture delivered at the Royal Institute of Public Health, May 9, 1917.

is for "improvements in the manufacture of 3·6 diamino acidine and its derivatives," which yields a yellow dye. The specification says—

"3·6-diamino-10-methylacridinium-chloride is very easily soluble in cold water, with a yellow colour and a slight green fluorescence, which increases considerably on heating or on dilution. Solutions in methyl- and ethyl-alcohol show a very intense beautiful green fluorescence."

Mr. Ellis, for Messrs. Levenstein, Ltd., explained that the honour lay with British doctors of having discovered that this substance provides the most notable antiseptic for war surgery forthcoming since Lister introduced antiseptic methods. Antiseptics hitherto, used in sufficient strength, have had the disadvantage of injuring the tissues of the body and "inhibiting the normal protective functions such as phagocytosis," according to the report on the action of Flavin presented to the Medical Research Committee by Dr. C. H. Browning, Dr. E. L. Kennaway, Dr. R. Gulbransen, and Dr. L. H. D. Thornton, from the Bland-Sutton Institute of Pathology, Middlesex Hospital. This historic report appears at length in the *British Medical Journal* of January 20 last, where it is followed by an article on the effects of its use at Middlesex Hospital, by the Assistant-surgeon of the Hospital, Dr. Ligat, F.R.C.S. The article is entitled "Flavine and Brilliant Green in the Treatment of Infected Wounds."

Mr. Potts, of Messrs. W. P. Thompson and Co., Liverpool, who appeared for Messrs. May and Baker, Ltd., said the problem in antiseptics had been to find a substance which had a specific or selective action on the disease germ and, together with a high toxic action on the parasite, had very little dangerous action on the body itself. The patent was first found to be useful for sleeping sickness. Before Dr. Browning and his collaborators made their experiments last year the whole science of antiseptics was in a very primitive state. What was wanted was something which would attack the disease germs on the surface of the body without affecting, or being affected by, the serum of the body, and something which would not reduce the activity of the phagocytes in the blood in repelling the disease germs. Other antiseptics, used strong enough to grapple with the disease germs, had a deleterious effect on the delicate tissues and lowered the power of the corpuscles of the blood to repel infection. It was like killing rats by asphyxiating gases, which also damaged the fabric of the house and reduced the legitimate occupants to impotence. Flavin had none of these injurious effects, and it actually increased the efficiency of the phagocytes. It sold at several shillings an ounce (the cost had always been fatal to the commercial use of the dye), but a solution of one part in a thousand parts of water (as employed by Dr. Browning) yielded a sufficiently powerful antiseptic. The strength at which it did its healing work was 400 times less than the strength which was harmful to the body. Over 1500 cases had been treated in fifteen months, and in one particular case, where a man had a piece of skin torn from the scalp, the size of a man's hand, the wound was entirely healed by Flavin in five days. Dr. Ligat said he had treated with it a number of shrapnel wounds, some 6 inches square, with universally successful results. A clean surface might be expected in five days, and the rapidity with which the epithelium grew in from the edges was a very noticeable feature.

According to the Bland Sutton Institute's report to the Medical Research Committee, "in the presence of serum Flavin is the most potent bactericide of all those investigated, for both staphylococcus and *B. coli*, and it is equally efficient for the enterococcus and for anaerobes such as *B. oedematis maligni*."

Messrs. Blandy Bros. and Co., it was stated, had been manufacturing for the Bland-Sutton Institute doctors, and the authorities had requested Messrs. Levenstein also to manufacture, and they had made the War Office a present of all they had made.

The Controller of Patents (Mr. Temple Franks) said the licences would certainly be issued, and it would be considered, in view of the vital public necessity for the preparation, whether they should be issued without a royalty. The name and brands by which the substance should be known would also have to be decided. Messrs. Levenstein had been supplying under the name of "wound antiseptic, AVVALIN brand."

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, May 10, 1917.

Sir J. J. THOMSON, O.M., President, in the Chair.

PAPERS were read as follows:—

"*Permanent Periodicity in Sun Spots.*" By Sir JOSEPH LARMOR, F.R.S., and N. YAMAGA.

A discussion of the more sharply marked phases of the curve of frequency of sunspots, since 1750, led Newcomb, in 1902, to strong confirmation of the prevalent view, previously verified by Wolf and by Wolfer, that sunspots are governed by some permanent periodic agency of period determined very closely by him as $11\cdot13 \pm 0\cdot02$ years, and more recent independent discussions—by Wolfer in 1902, and by Schuster in 1906—have led them to conclusions nearly identical. The form of this periodic component is here extracted by semigraphical methods, such as are appropriate to a permanent unbroken period, and which also provide a further check on the degree of validity of the result. The periodic feature is found to be strongly and definitely present, provided the records for the two sunspot cycles from about 1776 to 1798, which would largely vitiate it, are rejected as untrustworthy, or else are almost wholly assigned to some strong but transient anomaly. The residue of the sunspot curve, when this periodic part is removed, seems to be accidental and sporadic, showing no other permanent periodicity of comparable period. The periodogram analysis of Schuster had, in fact, already led him to the result that the record is not homogeneously constituted even in the wider sense appropriate to natural radiation. The Fourier series here determined for the periodic part is found to be composed of sines only within the limits of attainable accuracy; thus the graph of that part is made up of anti-symmetrical undulations, a feature which may form a clue to its physical origin in the sun.

"*High-Frequency Resistance of Multiple-stranded Insulated Wire.*" By Prof. G. W. O. HOWE.

The conductors employed in radio-telegraphy are frequently made up of a large number of fine wires separately insulated and stranded or plaited together in such a way that every wire occupies in turn the same relative position in the multiple conductor. In this way the total current is forced to distribute itself equally between all the wires, even at high frequencies. The object of this is two-fold, viz., to make the inductance independent of frequency and to reduce the resistance at high frequencies. It is shown in this paper that the second object is rarely achieved because of the eddy currents induced in the wires by the magnetic flux within the conductor. It is shown that the loss due to this cause is so great that the effective resistance of the stranded conductor is, in many cases, greater than that of the solid wire which could be put in its place.

In the first part of the paper formulæ are deduced on the assumption that the eddy currents in the fine wires do not appreciably affect the distribution of magnetic flux within them. In the second part this assumption is not made, and formulæ are deduced which take into account the screening effect of the eddy currents. It is proved, how-

ever, that the assumption is permissible in nearly all the cases considered.

A number of tables are given showing the ratio of the high frequency to the continuous current resistances of straight and coiled conductors of different sizes made up of fine wires of three alternative diameters. These formulæ and tables enable one to see at once if any advantage is to be gained by using such a stranded conductor in any given case, and, if so, the best number of wires and space-factor to employ. The paper shows conclusively, however, that the extended use of such conductors in radio-telegraphy for the purpose of reducing the resistance has no scientific justification.

PHYSICAL SOCIETY.

Ordinary Meeting, April 27, 1917.

Prof. C. V. BOYS, F.R.S., President, in the Chair.

A PAPER entitled "A Note on the Derivation of the General Equation for Wave Motion in an Elastic Medium" was read by Prof. J. A. FLEMING, M.A., D.Sc., F.R.S.

The paper explains a simple method of arriving at the general differential equation for wave motion, viz.,—

$$\frac{d^2\phi}{dt^2} = c^2 \left(\frac{d^2\phi}{dx^2} + \frac{d^2\phi}{dy^2} + \frac{d^2\phi}{dz^2} \right),$$

where c is the velocity of propagation of the wave. A wave motion consists in the propagation of some form of strain through an elastic dense medium or one having comparable qualities. Corresponding to this strain there is an analogous stress in the medium, and we can express this stress mathematically in two ways—viz., kinetically, as the product of the density and the time rate of change of the strain, or by $m \frac{d^2\phi}{dt^2}$ per unit of volume; and also statically as the space increment of the expression $e \frac{d\phi}{dr}$, where e is a coefficient of elasticity and r is a vector denoting direction of propagation. Hence, for plane waves we can write the equation—

$$m \frac{d^2\phi}{dt^2} \delta r = \frac{d}{dr} \left(e \frac{d\phi}{dr} \right) \delta r,$$

or if m and e are independent of distance, we have—

$$\frac{d^2\phi}{dt^2} = \frac{e}{m} \frac{d^2\phi}{dr^2},$$

which is the known differential equation of wave motion for plane waves. Its solution is—

$$\phi = F \left(x \mp \sqrt{\frac{e}{m}} t \right),$$

where F is some function. In the same manner for spherical waves originating in a point source we can write the stress equation—

$$4\pi r^2 m \frac{d^2\phi}{dt^2} = \frac{d}{dr} \left(4\pi r^2 e \frac{d\phi}{dr} \right) \delta r,$$

which at once gives—

$$\frac{d^2\phi}{dt^2} = \frac{e}{m} \left(\frac{d^2\phi}{dr^2} + \frac{2}{r} \frac{d\phi}{dr} \right);$$

or, if $r^2 = x^2 + y^2 + z^2$, we have—

$$\frac{d^2\phi}{dt^2} = \frac{e}{m} \left(\frac{d^2\phi}{dx^2} + \frac{d^2\phi}{dy^2} + \frac{d^2\phi}{dz^2} \right).$$

The solution of this last equation is—

$$\phi = \frac{1}{r} F \left(x \mp \sqrt{\frac{e}{m}} t \right),$$

where F is some function.

The general equation for electro-magnetic wave propagation in a pure dielectric may also be obtained in the same manner. In this case the strain on the medium is

the electric displacement D , and, if E is electric force, then on a system of rational units $1/K$, where K is the dielectric constant, is the electric elasticity. Hence we can consistently assume that the magnetic permeability μ corresponds to density, and then the kinetic measure of the electric stress is $\mu \frac{d^2 D}{dt^2}$, and this must be equated to the

space variation of the static measure of the electric stress.

For the spherical wave from a point source this leads to the equation—

$$\frac{d^2 D}{dt^2} = \frac{1}{\mu K} \left(\frac{d^2 D}{dx^2} + \frac{d^2 D}{dy^2} + \frac{d^2 D}{dz^2} \right),$$

with the solution—

$$D = \frac{1}{r} F \left(x \mp \frac{1}{\sqrt{\mu K}} t \right).$$

The wave is therefore propagated outwards without change of wave form; but the amplitude varies inversely as the distance from the source.

Since the Laplacean operator $\frac{d^2}{dx^2} + \frac{d^2}{dy^2} + \frac{d^2}{dz^2}$ is an invariant, and is not altered in form by a shift of origin; and since we can by Huyghens' principle consider a wave of any kind as the resultant of a set of spherical waves originating at various point sources, we can apply the above method to the case of wave motion generally.

The method above described may be epitomised by saying that we obtain the differential equation by equating the product of strain-acceleration $\frac{d^2\phi}{dt^2}$ and density to the

static measure of the stress expressed as the space variation of the product of the elasticity and the strain slope $\left(e \frac{d\phi}{dr} \right)$, which is the proper measure of the stress at the point considered.

DISCUSSION.

Mr. F. J. W. WHIPPLE thought that the validity of Prof. Fleming's application of Huyghens' principle might be questioned. In the first place, he thought that the principle itself required proof just as much as the property that it was used to establish. Further, the secondary wavelet from each point in a wave front was assumed to be spherical. Was it not the case that the phase of these disturbances was a function of the direction, relative to the main wave front, as well as of the distance from the origin of the wavelet? Another interesting question was how the equations would have to be modified in the case of the energy reflected at the boundary surfaces of the medium.

Prof. C. H. LEES did not quite see how Prof. Fleming's treatment of the problem differed from that given in Love's "Elasticity," for example.

Prof. J. A. FLEMING, in reply, wrote that the criticisms of the two speakers in the discussion rather missed the point of the paper. The validity of Huyghens' principle is not in question. Most writers on physical optics have resorted to it, and he (Dr. Fleming) had never seen any explanation of the phenomena of diffraction which did not rest upon it. The proof given in the paper that the characteristic equation proved for spherical waves with origin at the centre may be applied to waves however originating is made to rest upon the fact that the Laplacean operator is invariant with regard to origin. The object of the paper was not to write a complete theory of wave motion, nor of elasticity, but merely to give a method, which seems valid, for arriving immediately at the characteristic equation in a manner which would appeal to students not very well versed in hydrodynamics or the theory of elasticity. Prof. Lees asks how far the treatment differs from that given, say, in Love's "Theory of Elasticity." The answer is not at all in the result; but the method used in the paper enables us to arrive by simple considerations at the characteristic differential equation, and then to elucidate the physical meaning of its solution. It seems better for a physical and engineering student to

have some approach to such conception rather than none at all. The treatment of the subject of wave motion is generally very difficult to follow in advanced text-books, whereas the practical applications of sound, water, and electromagnetic waves makes some theoretical knowledge of the subject necessary.

A paper entitled "*The Effect of Stretching on the Thermal Conductivity of Wires*," by A. JOHNSTONE, B.Sc., was read, in the absence of the author, by Prof. C. H. LEES, F.R.S.

In the experiments carried out, the wire to be tested was fixed at each end between the jaws of screw clamps joined to brass cylinders, through which water could be circulated. Attached to one clamp was a rod passing through a framework, enabling tension to be applied by a nut working on a thread.

Heat was supplied to the centre of the wire by passing a current of electricity through a manganin coil wound on the wire, and the temperature difference between two points on the same side of the centre was ascertained by two platinum coils, also wound on the wire.

The resistances of the coils were determined by means of a Callendar-Griffiths bridge, enabling a temperature difference of 0.01° C. to be read, and making it possible to detect a difference in conductivity of 0.05 per cent. If R_1 is the resistance of the platinum thermometer nearer the heating coil, and r_1 is that of the other platinum coil when both are at the jacket temperature; and if R_2 and r_2 are corresponding values when a temperature difference exists, then it may be shown that the conductivity—

$$K \text{ is proportional to } \left(\frac{R_2}{R_1} - \frac{r_2}{r_1} \right)^{-1}.$$

For all the wires used (copper, steel, nickel, aluminium, brass, zinc), stretching produced a slight increase in thermal conductivity. The most satisfactory experiments showed an increase of about 0.5 per cent for a tension of about 0.7 of the elastic limit.

After the tension was withdrawn the conductivity returned approximately to its original value.

DISCUSSION.

Mr. F. E. SMITH suggested that it would have been of interest if the author had made simultaneous observations of electrical conductivity on the same apparatus. Had any experiments been made on liquids, such as mercury, for example?

Prof. BOYS asked if the coefficient would be reversed if compression were applied instead of extension. He realised there would be some practical difficulties in making the experiments.

Prof. LEES, in reply, said that there would have been electrical measurements included in the paper but for the author's absence in the Army. He thought compression measurements could be made, though they had not, so far, been carried out.

A paper on "*Cohesion*" (Third Paper), by Prof. HERBERT CHATLEY, D.Sc., was taken as read.

The objects of the paper are:—

(a) To re-state and add further evidence in favour of an electrical theory of cohesion.

(b) To provide tentative empirical formulæ for the expression of inter-molecular forces.

The author defines cohesion as the net attraction (i.e., balance of attraction over repulsion) between molecules which are relatively chemically saturated, at distances not greatly exceeding the molecular diameters, and the following formula is proposed for this attraction:—

$$t_2 = Gm^2/d^{(2+4d_0/d)},$$

where G is the Newtonian constant of gravitation, m the molecular mass, d the molecular interval (centre to centre), and d_0 is the molecular diameter.

DISCUSSION.

Dr. R. S. WILLOWS (communicated remarks) pointed out that the statement that an electrified liquid evaporated more quickly than a neutral one is not true in all cases. C. T. R. Wilson's fog experiments show, for small drops, that evaporation is most rapid when the drops do not contain an electric ion.

NOTICES OF BOOKS.

The City of Nottingham; Past, Present, and Future.

Officially issued by the Corporation. 1917. Pp. 56.

THE city of Nottingham possesses many advantages from an industrial point of view, and the Industrial Development Department announce that there are many sites available for the erection of new works, which they trust will attract manufacturers who are interested in fostering the growth of the chemical industries of our country. It is pointed out that in particular there is room for margarine works, beet sugar works, and works for the manufacture of glass bottles. The city is readily accessible from all parts of England by rail and water ways, and, owing to the excellent municipal system, the rates compare very favourably with those of similar towns. The short accounts given in this book of the rise and present states of the principal industries and trades show that they are in a uniformly flourishing state, and under the management of the obviously efficient and alert Industrial Development Department a steady growth in the size and prosperity of the city may be expected with confidence.

Oxford University Press. General Catalogue. November, 1916. Oxford, London, New York, Edinburgh, Toronto, Bombay, Melbourne, Glasgow, Cape Town, Madras, Shanghai: Humphrey Milford. Pp. viii+566.

THIS catalogue of the publications of the Oxford University Press is much more than a mere list of books and prices, and will be found to be a possession of permanent value. The books catalogued are divided into six sections:—General Literature, Modern History and Law, &c., English and other Modern Classics, the Ancient World, Natural Science and Medicine, and Bibles and Devotional Books. Details are given of the contents of the volumes, besides price, size, date of publication, &c. In addition there is a complete alphabetical index to all authors and some titles.

CORRESPONDENCE.

DETERMINATION OF TIN.

To the Editor of the Chemical News.

SIR,—May I trespass on your "Correspondence Column" to ask any of your readers for a speedy and accurate method for determining the percentage of small amounts of tin (say, 0.5 per cent Sn) in tungsten powder (say, 98.0 per cent W)?—I am, &c.,

H. B. COHEN.

Sheffield.

MEETINGS FOR THE WEEK

TUESDAY, 29th.—Royal Institution, 3. "The Flow of Ice and of Rock—The Movement of Glaciers," by Prof. W. W. Watts, F.R.S.

THURSDAY, 31st.—Royal Institution, 3. "The Art of the Essayist," by A. C. Benson, C.V.O.

FRIDAY, June 1st.—Royal Institution, 5.30. "The Brontës—a Hundred Years After," by J. H. Balfour Browne.

SATURDAY, 2nd.—Royal Institution, 3. "The Electrical Properties of Gases," by Prof. Sir J. J. Thomson, O.M.

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VOLUMETRIC DETERMINATION OF SULPHUR IN PYRITES.

By T. J. I. CRAIG, D.Sc.

Introduction.

MANY analysts have investigated and proposed various methods of ascertaining the percentage of sulphur in pyrites. In cases of any importance pyrites samples are almost invariably tested for sulphur by gravimetric analysis; the sulphur being converted into sulphuric acid and then precipitated and weighed as barium sulphate. Simple as this method appears to be, it is hedged round by several sources of error, and much controversy has been published by one and another as to this or that modification giving the most accurate result.

A reliable and simple volumetric method which at the same time is fairly rapid would be decidedly useful.

The author of this paper being in a laboratory where many samples of pyrites are regularly analysed by gravimetric methods, and the reduced staff becoming hard pressed for time owing to the European War, looked about for a suitable accurate volumetric method which would assist in obtaining the results more rapidly and with at least equal reliability.

The idea arose that after dissolving the pyrites in aqua regia (or by other suitable method) it might be possible to eliminate all acids other than sulphuric acid and determine the latter by titration with standard alkali. Investigations were carried out, and it was found to be quite feasible, when using aqua regia as solvent, to completely remove in the course of the analysis, first the nitric acid, then the hydrochloric acid, and finally the arsenic acid, leaving only the sulphuric acid, for the determination of which a rapid and accurate method was worked out on the above lines. Subsequent experiments showed that a more convenient method of attacking the pyrites is to treat it with dilute nitric acid, and finish off by adding a few cc. of bromine and boiling until all excess bromine is eliminated. By this means no hydrochloric acid is introduced, all the bromine is boiled out, and the nitric acid is practically completely eliminated on taking to dryness, moistening with water, drying again, and heating for some time at 110° C.

Accounts are hereinafter given of experimental investigations carried out with regard to the aqua regia method of oxidation, and also the dilute nitric and bromine method, which latter appears to be a new suggestion.

Historical.

G. Lunge goes pretty fully into the gravimetric (BaSO_4) method, beginning on p. 89 in vol. i. of the 4th (1913) edition of his well-known publication on "Sulphuric Acid and Alkali"; W. S. Allen and H. B. Bishop read a comprehensive paper on this method to the Eighth International Congress of Applied Chemistry (vol. i., Sect. 1, p. 33); and in 1915 H. C. Moore also thoroughly investigated the method and published the results in the *Trans. of Ind. and Eng. Chemistry* (vii., No. 7, p. 634).

Other investigators who have taken the matter up are:—Gladding (*Journ. Am. Chem. Soc.*, 1896, [5], xviii., 446, and *Journ. Soc. Chem. Ind.*, xv., 617); Pattinson (*Journ. Soc. Chem. Ind.*, xxiv., 7); the Committee of the Chemical Society of North France, who reported to the Fifth International Congress of Applied Chemistry, Berlin (*Zeit. Angew. Chem.*, 1903, [23], xvi., 541); Knorre (*Chem. Ind.*, 1905, xxviii., 2); and E. T. Allen and Johnstone (*Journ. Ind. Eng. Chem.*, 1910, ii., 196).

Lunge refers to several volumetric methods proposed by various authors, but does not find a satisfactory usefulness in any of them. Wilderstein (*Zeit. Anal. Chem.*, i., 432) was the first to propose that sulphuric acid might be determined by a standard solution of barium chloride. Teschemacher and Smith (*CHEMICAL NEWS*, xxiv., 61) took up the same idea, especially for the analysis of pyrites. Compare also Glendinning and Edgar (*Ibid.*, p. 140). C. and J. Beringer introduced the addition of sodium acetate and acetic acid into this titration (*CHEMICAL NEWS*, lix., 41). Lunge refers to various other methods proposed by Mohr, Cleum, Wilderstein (second method), Schwartz, and Pappenheim, and which are described in the treatise of Fresenius and Mohr. The method proposed by Wilsing (*Chem. Ind.*, 1886, p. 25) has a slight but apparently useful modification of those just mentioned. L. W. Andrews (*Am. Chem. Journ.*, 1889, p. 567) proposed to determine sulphuric acid combined with bases by adding a solution of pure barium chromate in hydrochloric acid to the hot dilute sulphate solution, and then ammonia, and filtering of the liquid now containing chromate equivalent to the SO_3 . The chromate is determined by means of potassium iodide and decimolal thiosulphate. U. S. Borge and T. Sotgia (*Atti. v. ist. Veneto*, 1912, lxxii., [2], 1097, and *Chem. Abs.*, x., 1308) publish a modification of Andrew's method. Reuter (*Chem. Zeit.*, 1898 p. 357) and Marbounin and Moulinié (*Chem. Centr.*, 1898, i., 218) describe similar analytical processes. Raschig (*Zeit. Angew. Chem.*, 1903, [24], xvi., 818) determines sulphur in pyrites by dissolving in aqua regia, drying, boiling for five minutes with 50 cc. of 1 per cent hydrazine hydrochloride, diluting to 250 cc., pouring 50 cc. into 400 cc. benzidine solution, filtering after five minutes, washing with not more than 20 cc. H_2O , and titrating the precipitate with N/10 alkali and phenolphthalein. Zehetmayer (*Zeit. Angew. Chem.*, 1910, xxiii., 1159) proposed to heat pyrites with metallic iron, treat the result with HCl, and titrate the H_2S given off by means of iodine and thiosulphate.

E. Martin (*Monit. Scient.*, 1913, iii., 686) gives the following method:—

The ground sample (0.5 grm.) is treated with aqua regia (25 cc.), and after several hours sodium chloride (1 grm.) is added and the mixture evaporated to dryness. The residue is treated with HCl (1 cc.), 50 cc. boiling water are added, and then sodium carbonate (4 grms.) in small portions at a time. The filtered solution is made neutral to methyl-orange, and boiled to expel CO_2 . 60 cc. of $\text{Ba}(\text{OH})_2$ solution (45 grms. per litre), and some phenolphthalein are added, CO_2 is passed through until the colour is just discharged, the precipitate is filtered off, washed with warm water, and the filtrate after cooling is titrated with N/2 HCl.

Further details are given of certain precautions necessary to the method (*Monit. Scient.*, 1914, iv., 86). Considerable excess of Na_2CO_3 must be present, and the CO_2 used should be just enough to discharge the phenolphthalein pink colour.

Several methods have been proposed for determining the available sulphur; e.g., W. G. Mxter (*Am. Chem. Journ.*, ii., 396) burns the pyrites in a current of oxygen and passes the vapours into a mixture of barium and hydrochloric acid. Lunge suggests using neutral hydrogen peroxide to absorb the vapours and then finding the total acidity by titration with alkali. He gives a complete list of methods on these lines, and they appear in his "Sulphuric Acid and Alkali," 4th edition, p. 100 et. seq.

Various methods have been proposed for obtaining pyrites sulphur in the form of SO_3 . The finely-ground pyrites may be dissolved by means of fuming nitric acid, aqua regia, potassium chlorate and hydrochloric acid, or potassium chlorate and nitric acid. Lunge himself recommends aqua regia (1 HCl to 3 or 4 HNO_3), using 50 parts per 1 of pyrites. Some chemists recommend a solution of bromine in hydrochloric acid. Lunge, however, has found this to be unsuitable. Drown (*CHEMICAL NEWS*, xliii., 89) heats the pyrites with 1.25 sp. gr. NaOH, adds bromine,

then HCl, and takes to dryness. Noaillon (*Zeit. Angew. Chem.*, 1897, p. 351) uses NaClO_3 and HNO_3 . Allen and Bishop (*loc. cit.*) recommend oxidation of the pyrites by means of a mixture of 2 parts by volume of liquid bromine and 3 parts of carbon tetrachloride (free from S), then in fifteen minutes 15 cc. HNO_3 are added, and after another fifteen minutes gentle heat is applied till all action ceases and the solution is evaporated to dryness and treated with HCl as usual.

Fresenius (*Zeit. Anal. Chem.*, xvi., 335) prescribes to decompose pyrites in the dry way by fluxing with 20 parts of a mixture of 2 parts anhydrous Na_2CO_3 (free from S), and 1 part KNO_3 , but according to Lunge this process and its subsequent treatment is much more troublesome and tedious than the wet way oxidation by means of aqua regia. Moreover, the sulphur of the galena and barium sulphate which are useless to the manufacturer are determined with the useful sulphur which is combined with the iron and copper. Gladding describes a comparison of the fusion and aqua regia methods (*Journ. Am. Chem. Soc.*, xvi., 398).

To obtain the sulphur of the pyrites in solution the author for the first series of experiments employed the well known method described by Lunge of treating the finely-ground ore with aqua regia. The weighed portion of the sample is first treated with the HCl (1 part), then the HNO_3 (3 parts) is poured in, and the mixture gently warmed till action commences. It is then set aside away from the heat till the action is over, after which the vessel is returned to the steam-bath and left covered up till all action ceases, and the solution is then allowed to evaporate to dryness. Hydrochloric acid is now added and evaporation to dryness again carried out. Finally, the dried mass is heated to 110°C . for one hour, and then dissolved in distilled water, and the insoluble matter is filtered off and washed.

For those who prefer it, the solution method of Allen and Bishop may be adopted. The author, however, was not favourably placed for obtaining a suitable sulphur free carbon tetrachloride, and therefore employed the aqua regia method, which was always found quite satisfactory, at all events so far as concerns the dissolving of the sulphur.

It was observed in the Allen and Bishop method of attack that no bromine was left in the dried residue, thus leaving only nitric and arsenic acids to be removed in order to obtain the sulphuric acid as the only acid which would be determined by the titration with standard alkali and phenolphthalein as indicator.

A few experiments were made to observe the behaviour of nitric acid alone on finely-ground pyrites, and it was found that strong HNO_3 acted with great violence and much frothing. By diluting the HNO_3 with its own volume of distilled water the action went on smoothly and quite energetically enough. A noticeable amount of sulphur was left undissolved. It was found, however, that this sulphur could be easily and completely dissolved by cooling the liquid to about 50°C ., adding a few cc. of bromine, and shaking round for a minute or so; the bromine gathered up the sulphur, and by adding a little more HNO_3 and bringing to the boil complete oxidation took place. The solution dried quickly, leaving a residue from which all the nitric acid could be driven out by thoroughly drying on the steam, moistening with water, and drying again, and then heating for an hour in the air-bath at 110°C . This method was finally adopted, and is recommended for dissolving pyrites to obtain a solution containing the useful sulphur in the form of neutralisable sulphuric acid which could then be determined by titration with standard alkali and phenolphthalein as indicator in the manner hereinafter described.

It is recommended also as a satisfactory method of dissolving pyrites for gravimetric determination of the sulphur.

Pyrites, FeS_2 , when dissolved in aqua regia yields ferric sulphate and free sulphuric acid:—



Natural pyrites as used for sulphuric acid manufacture usually contains sulphur in excess of that required to form normal salts with the bases which are present, and thus there is a certain proportion of free sulphuric acid after the oxidation by means of aqua regia or other such method in which no extraneous bases like alkalis have been introduced. This free acid assists in expelling the volatile acids when the solution is taken to dryness.

It is well known that all the nitric acid can be eliminated from the aqua regia solution of pyrites by adding HCl and evaporating to dryness. To remove all the hydrochloric acid is not so easy, as even after repeated evaporations with water a small yet appreciable amount clings to the residue. The author finds, however, that this HCl is completely removed from the solution by the addition in the cold of pure moist silver oxide. The resulting silver chloride may be easily filtered off and washed quite free from SO_3 , and thus solution of pyrites can be obtained containing all the useful sulphur in the form of neutralisable SO_3 , and free from other acids with the exception of arsenic acid when arsenic acid is in the pyrites. This arsenic acid (as will be subsequently demonstrated) is carried out of the sphere of action in an insoluble inactive form united with or adhering to the ferric hydrate which is formed when the solution is being neutralised with standard alkali. Lockemann and Pauke (*Zeit. Chem. Ind. der Kolloide*, 1911, viii., 273) have shown that ferric hydrate precipitated by ammonia completely removes small amounts of arsenic from solution. They state that this property is diminished when soda or potash is used instead of ammonia, and give as their view of the cause that the ferric hydrate takes up a large amount of alkali and thereby the attraction for arsenic is lessened. The author of this paper, however, has investigated this point, and finds that ferric hydrate precipitated in the cold by a small excess of fixed caustic alkali retains only a slight amount of the latter, which is completely dissociated on boiling with water. It would appear to be more likely in the case of Lockemann and Pauke that the weakened adsorptive power for arsenic is due to the greater affinity of the arsenic for the excess of free alkali in solution. The author finds that with a relatively large amount of iron present and no great excess of alkali there is substantially complete removal of the arsenic by the ferric hydrate. In this way the arsenic acid is rendered inert and is not determined with the sulphuric acid. After dissolving the pyrites any sulphur combined with barium and lead (and therefore useless to the manufacturer) will be found in the insoluble matter as barium and lead sulphate, and these are filtered off. If calcium is present in the pyrites it will form calcium sulphate, and a part of it at all events will be soluble, and in gravimetric determinations will increase the BaSO_4 to a certain degree. Lunge (*Journ. Soc. Chem. Ind.*, iv., 31) has given the solubility of CaSO_4 in different strengths of HCl; e.g., 100 cc. of a 3 per cent HCl solution dissolve 1.26 grms. CaSO_4 at 25°C .

By the herein proposed volumetric method, any such sulphuric acid combined with calcium (and therefore representing useless sulphur) will not be determined even although in solution, and therefore this test gives a result fairer from the manufacturer's point of view. (See Lunge, *Journ. Soc. Chem. Ind.*, iv., 449, 924).

Maurice de Lummen in a paper on "The Roasting of Blende" in the *Chemical Trade Journal* (May 18, 1916, No. 1504, lviii., 255), describes the behaviour of compounds of zinc, lead, iron, calcium, magnesium, barium, and fluorine when mineral sulphides containing such are roasted. With reference to zinc sulphides Lunge states that with well conducted roasting all the S passes off mainly as SO_2 and a little as SO_3 . Lead sulphide goes into sulphate, iron sulphide is entirely decomposed, and all the S comes off.

If lime is present it goes into sulphate in the burning of the pyrites; so also with barium and magnesium. Lunge, however ("Sulphuric Acid and Alkali," 1903, i., 77, Part I., Third Edition), reckons that sulphur combined with zinc

in pyrites is useless for SO_3 making, as the sulphate of zinc is not decomposed at the temperature of a pyrites burner, and further states that in France half of the S combined with zinc is considered as lost, and for copper they reckon 0.505 per cent S per 1 per cent Cu as lost.

There would thus appear to be some uncertainty as to what really happens to the sulphur united with zinc and copper in pyrites when the latter is roasted. The sellers of pyrites have therefore some excuse for claiming payment for such sulphur but none for including Sequivalent to the lime which may be present.

So far as the author has been able to ascertain no one appears to have published a volumetric method of determining sulphur in pyrites on the lines of taking the aqua regia or similar solution and titrating it with standard alkali.

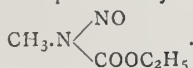
To be continued).

DIAZOMETHANE.

By F. H. LORING.

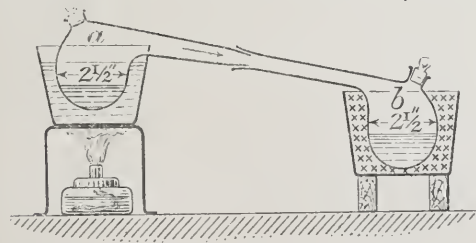
THE preparation of diazomethane, $\text{CH}_2 \begin{smallmatrix} \diagup \text{N} \\ \parallel \\ \diagdown \text{N} \end{smallmatrix}$, may be of interest.

Referring to the accompanying sketch, into the retort *a* place 2.5 cc. of nitrosomethylurethane. This substance is a liquid, and may be represented by the formula—



Add thereto 25 cc. of pure dry ether, or ether of specific gravity 0.72. Finally, add 1.75 cc. of alcoholic solution of caustic potash (KOH dissolved in four times its weight of methylic alcohol). This may be a milky saturated solution.

Distil the bulk of the contents of *a* over into the receiver *b* by means of the hot water and the ice and



calcium chloride baths as shown. In *b* a pale intense yellow liquid condenses, the yield being about 50 per cent of the theoretical quantity.

It may be found desirable to cool the necks of the retort and receiver by applying cold wet cloths.

The nitrosomethylurethane was purchased from Germany, as the experiment was made some years before the war, after reading Von Peckman's paper (*Ber.*, 1895, xxviii., 855). Von Peckman refers to the nitroso compound in the following words:—

"Nitrosomethylurethane.—Klobbie got this combination discovered by him through treating urethane with nitrite and sulphuric acid. For the manipulation of large quantities of this body it is more judicious to conduct the red vapours developed through arsenic and sulphuric acid while cooling the same when passing into the rarefied pure urethane with an equal volume of ether till the fluid has assumed a dirty grey colour. Then it is washed with water and soda, dried with sodium sulphate, and finally rectified in a vacuum. The latter is not a necessary procedure when preparing diazomethane. In working with the nitroso combination one cannot be too careful, on

account of its danger already mentioned by Klobbie, to skin, lungs, and eyes. . . . The substance causes on the skin red itching spots and blisters. The inspiration of its sweetish smelling vapours produces stubborn bronchial catarrh, as well as painful inflammation and disturbance of accommodation of the eyes. . . . Since the accompanying appearances are not unlike the symptoms of diazomethane poisoning, the conjecture suggests itself that the poisonousness of nitrosomethylurethane depends on the change into diazomethane taking place on the organism."

In the same paper Von Peckman speaks of diazomethane as follows:—He says that the etheric solution (substantially as prepared above) is intensely yellow at a strength of from 3 to 5 per cent. "At ordinary temperatures diazomethane is a yellow gas which can be condensed by cold after a preliminary attempt. To this end the procedure was as above, but instead of ether water-free glycerin was employed, and through the whole system a stream of hydrogen was passed; the disappearing gases left behind in a snow chloride of calcium mixture dark yellow little drops which, when removed from the freezing mixture, were in active boiling at about 0° C."

Caution.—The nitroso compound and the diazomethane are highly poisonous substances, and the vapours therefrom should not be allowed to come into contact with any part of the body or face. One or two whiffs of the vapours from the etheric solution of diazomethane striking the fingers may render them so tender in two days that it will be difficult to pick up a pin. The greatest precautions are therefore necessary when handling such poisonous substances.

SOME MAIN LINES OF ADVANCE IN THE DOMAIN OF MODERN ANALYTICAL CHEMISTRY.*

By A. CHASTON CHAPMAN.

ANALYTICAL chemistry has often been referred to as the handmaiden of the other branches of our science, and whilst this was an entirely unobjectionable description in so far as it implied indispensable assistance, it was a little unfortunate in that it carried with it a certain suggestion of inferiority. From the dawn of scientific chemistry in the seventeenth century to a period within the recollection of a good many chemists who are still happily among us, analytical chemistry was almost synonymous with chemistry itself, and it is only in comparatively recent times that it has become a separate branch of applied chemistry with its own literature, its own aims, and its own specialised practitioners. Whilst the division of chemistry into various separated branches became inevitable with the enormous development of the science, and had its obvious conveniences, the progressive subdivision of work has not been without its drawbacks, and even its dangers. That it has conducted to a narrowness of outlook and to a mental onesidedness is undeniable, and it is becoming increasingly difficult always to maintain a just sense of proportion to view facts in their true perspective and to keep a firm hold on fundamental principles. Of all the various members of the body chemical, perhaps none suffered more at first by this process of subdivision than analytical chemistry. During the first half of the last century, chemical analysis occupied a very high position, since not only was it clearly the foundation-stone on which the whole chemical fabric was built, but almost every chemist of distinction practised it assiduously and devoted much of his time to a study of its problems. One need only recall in this connection such names as those of Berzelius, Gay-Lussac, Marignac, Bunsen, Dumas, Stas, Liebig, and Wöhler. With the birth of modern organic chemistry and its colossal development during the past

* A Lecture delivered before the Chemical Society, March 15, 1917.

half-century—a development which, be it remembered, was largely dependent in the beginning on the analytical labours of Gay-Lussac, Liebig, Dumas, and other early workers in the field—the analytical branch of our science was gradually relegated to a comparatively humble position. In the presence of this new and fertile field, in which every thrust of the spade served to bring to light some discovery of the highest importance and of the most absorbing interest, it is scarcely to be wondered at that the great majority of chemists should have forsaken the older branch, and that the all-important foundation-stone should have tended to become regarded more and more as merely the useful handmaiden. That the lamp of analytical chemistry was kept well alight during the period in question, notwithstanding the superior attractions of organic chemistry, is evidenced by the epoch-making researches of Bunsen and Kirchhoff on the spectrum analysis, by numerous records of observations on the qualitative electrolytic decomposition of metallic salts, on which the important branch of electrochemical analysis was later on to be founded, chiefly by the labours of Classen and his students, and by the many investigations having for their object the perfection and simplification of methods of gas analysis. Last, but not least, I may mention in this connection the establishment of the Fresenius Laboratory in Wiesbaden in 1848, and a few years later (1862) the foundation of the *Zeitschrift für Analytische Chemie*, the first journal, I believe, which was devoted exclusively to the interests of analytical chemistry. Our own journal, *The Analyst*, did not appear until 1877.

Great as is the temptation, it is not my intention to deal at any length with the history of analytical chemistry during the latter half of the nineteenth century. I will merely content myself with remarking that at a certain point in that history the rate of progress in its scientific development had slowed down so considerably that any chemist taking a superficial survey might well have been justified in supposing that future advances would be restricted to improvements in existing methods and to the extended application of those methods to the solution of new technical and industrial problems. That new lines of progress would be opened up must have seemed highly improbable, and it is recorded that a certain distinguished German chemist went so far as to utter the dictum that analytical chemistry presented no further problems. My task this evening will be to indicate briefly a few of the main lines along which the scientific development of modern analytical chemistry has proceeded, and to deal—however inadequately—with what I conceive to be the main causes of its restoration to something of its old position as a living and progressive part of our science. Foremost among these causes has unquestionably been the almost unparalleled growth during comparatively recent years of that younger member of the chemical family—I mean physical chemistry. That a proper understanding of analytical chemistry, as of every other department of the science, is dependent on a knowledge of those fundamental laws which it is the special province of physical chemistry to elucidate will appear to most chemists of to-day a self-evident proposition. Yet it was not until the publication of Ostwald's "*Wissenschaftlichen Grundlagen der Analytischen Chemie*" in 1894 that this all-important truth was presented to the chemical world, and not until some years later that it received anything like general recognition—at least in this country. To many generations of students chemical analysis has been taught as a useful art, consisting largely of a series of recipes which if followed conscientiously would usually lead to the desired result. Those recipes had often the authority of great names behind them, and so far as they went were admirable; but how many of those students were taught anything of the underlying principles, or were put by their teachers in a position to make for themselves such modifications of the orthodox processes as might at times become necessary? The result was to manufacture a body of more or less mechanical hand workers, and if, as fortunately happened, a

number of these showed initiative and developed originality, it was in spite of, rather than in virtue of, the instruction they had received. This state of affairs was, however, inevitable, since, as Ostwald has pointed out, it was only with the advent of the general theory of chemical reactions and states of equilibrium that it became possible to elaborate a theory of analytical reactions and to place analytical chemistry on a really scientific foundation. It was then the beneficent work of physical chemistry to infuse new life into analytical chemistry, to help to place it on a firm and wide basis, and to do much to remove the reproach that this branch of chemical science, whilst representing a useful field of highly skilled manual labour, could scarcely be regarded as an intellectual occupation.

In three main directions this revivifying influence has made itself felt during the past twenty years. In the first place, it has supplied the explanation of a vast number of facts which had been arrived at empirically, and are of the greatest importance to the analyst; in the second place, it has greatly stimulated and directed original research, and, finally, it has enriched analytical chemistry with a number of new appliances and has resulted in the introduction of many new methods of inquiry.

Of all the theories of modern physical chemistry, none has had so far-reaching and important an effect on the development of analytical chemistry as those connected with the nature of solution. It is not, in fact, going too far to say that the general adoption of these theories and their application to analytical processes was the means of placing analytical chemistry for the first time on a really scientific basis. The years 1885, 1886, and 1887, which for chemists will ever be memorable for the publication of the great generalisations of van't Hoff and Arrhenius, may justly be regarded as dates of outstanding importance in the history of analytical chemistry. To deal with this aspect of the subject at any length before an audience of chemists is quite unnecessary. That the theory of electrolytic dissociation has not met with universal acceptance is of little importance from this point of view, for I believe that even those chemists who regard it with the greatest disfavour would be inclined to admit that no other theory is able to explain so much or is capable of welding the whole chaotic mass of analytical phenomena into such a coherent and harmonious whole.

The manner in which it has contributed to the building of a serviceable, if not complete, theory of indicators, and its helpfulness in explaining the phenomena of electrolysis, hydrolytic dissociation, and mass action, are too well known to need more than a passing reference.

As a further instance of the fruitfulness of this concept and of its value to analytical chemistry I may mention the application of the conductivity method to the determination of the point of neutrality of liquids. This method, first suggested by Küster and Grüters in 1903, has since received a considerable amount of attention at the hands of a great many workers, and the numerous contributions to the subject by Sørensen, Michaelis, and others represent a storehouse of very valuable information in connection with the applicability of certain indicators to special purposes, the preparation of solutions of standard reaction, and the electrometric measurement of hydrogen-ion concentration. This work, which is undoubtedly capable of further development, has already proved of very great value in the investigation of certain bio-chemical problems, and will, no doubt, find extended application in the wider field of technical analysis.

In further exemplification of the close and fruitful connection between physical chemistry and analytical chemistry, I may just refer to the vast amount of work which has been done during comparatively recent years in connection with the colloidal state of matter and in the study of catalytic phenomena.

As showing, moreover, how some of the more recondite physical properties of matter may prove to be of practical importance to the analyst, I may perhaps be permitted to refer to the papers which I have published alone or in

collaboration with H. D. Law on the reducing action of hydrogen in its relation to analytical processes. In those papers it has been shown that much depends on the nature of the metallic surface from which the hydrogen is evolved. Thus, certain specimens of zinc which, owing to the presence of small quantities of impurities, are useless for the purpose of detecting and estimating minute traces of arsenic by the modified Marsh-Berzelius method, can usually be made suitable by coating the zinc with pure cadmium, thus producing a surface from which the hydrogen is evolved in a state of higher chemical activity.

In the same way, when an electrolytic method of estimating traces of arsenic is employed, much greater sensitiveness is obtained by using a lead or a cadmium rather than a platinum cathode. It is, of course, tolerably certain that the reducing efficiency of hydrogen, whether obtained by the interaction of metal and acid or by an electrolytic process, is dependent upon a number of factors, partly chemical and partly physical, and that the reactions are, in point of fact, very complex. There can, however, be very little doubt that among these factors the question of "potential" or "overvoltage" plays a prominent and important part.

The effect of employing cathodes of different metals in the reduction of arsenious oxide is shown by the following results:—

Cathode	Arsenious oxide added.	Arsenious oxide found.	Arsenious oxide left in flask.
Lead	10	10	—
Cadmium	10	10	—
Tin	10	10	—
Copper	100	10	90
Silver	50	10	40
Nickel	40	20	20
Platinum (black) ..	1000	0	1000
Iron	50	5	45

From this it will be seen that even the overvoltage of metals—a subject which at first sight might appear to be mainly of academic interest—has, in fact, a very direct and important bearing on some of the everyday operations of the analytical laboratory.

Time forbids that I should deal at any greater length with this side of the intimate relationship existing between these two branches of our science, and I will now refer briefly to the service rendered by physical chemistry in the direction of increasing the analyst's equipment and of multiplying his means of attack.

To the balance, the microscope, and the spectroscope there have been added from time to time a number of other physical instruments, some of which have revolutionised many of the older branches of analytical chemistry and have even been the means of giving birth to new ones. Whilst in its cruder forms the polariscope goes back to the beginning of the last century, or even beyond, the modern polarimeter is of comparatively recent birth, and since the introduction of the Jellet instrument about 1860, the labours of physicists and opticians have been almost continuously devoted to the perfecting of this highly important analytical appliance. Without it, carbohydrate analysis would to-day have been in a very different position, and many of the problems which confront the analyst in connection with the sugar, starch, confectionery, essential oil, and brewing industries would have been impossible of solution. In addition to these main applications of the polarimeter, there are many others of less importance, and new ones without doubt remain to be discovered.

Next perhaps in importance comes the refractometer, an instrument which finds wide and ever-increasing application in the analytical laboratory. What the polarimeter is to carbohydrate analysis the refractometer is to the analysis of fats and oils, and its assistance has been successfully invoked in the examination of brewing materials, milk serum, sugars, methyl and ethyl alcohols, glycerol, and many other natural and artificial products.

The calorimeter in all its forms and with all its modern refinements, as well as the various mercurial, resistance, and thermo-electric heat-measuring instruments, represent another section of what, for want of a better term, may be called analytical procedure, for the development of which the chemist is chiefly indebted to the physicist.

In addition to these physical instruments of almost everyday use, passing reference may be made to modern spectrographic apparatus, appliances for the determination of electrical conductivity, instruments for the measurement of colour and of turbidity, and, lastly—and of most recent introduction—apparatus suitable for making estimations of radioactivity.

I think I have said enough to show the general nature of the relationship existing between physical and analytical chemistry, and to indicate one of the main lines along which the latter branch of our science has advanced during comparatively recent years. Such indeed is the intimacy of the connection that, as new discoveries are made by physical chemists, they will almost inevitably be utilised in the consolidation or extension of that great field of analytical chemistry in which so many of us are proud to labour.

(To be continued.)

ON A UNIQUE OCCURRENCE OF MOLYBDENUM IN NATAL.

By ALEXANDER LOGIE DU TOIT, B.A., D.Sc., F.G.S.

DURING the course of the prospecting which took place some ten years ago in the Hlatimbe Valley, a tributary of the Umkomaas River, in Impendhle County, Natal, an occurrence of ores of molybdenum was noticed in association with the oil shales, the mineral being present not in quartz veins carrying crystallised molybdenite—its normal habit—but as an impregnation in coarse sandstone belonging to the Molteno division of the Karroo System and of Upper Triassic age.

The habit, therefore, is so unusual that a brief account of the ore-body will no doubt be of interest to mineralogists; indeed, so far as can be judged from a study of the available literature upon the distribution of molybdenum ores, this deposit is unique.

The precise locality is on the right hand side of the Hlatimbe Valley, and situated just within the area of Crown Land in the angle between the boundaries of the farms Memala and Duart Castle, below the escarpment of the Drakensberg.

The sandstone in question is the identical horizon which has been mapped continuously from the Stromberg in the Cape, and known as the Indwe Sandstone. It is only 18 feet in thickness here, but its lithological individuality still persists; at the top it is soft, medium-grained, and generally with glittering grains of quartz, while the lowest 4 or 5 feet is harder and coarser-grained, carrying small pebbles of white or grey vein-quartz sometimes as much as an inch across. The two parts are separated by a slightly uneven surface, along which are lenticles of extremely well laminated black shale set sometimes sparsely, at other times close together.

The sandstone stratum rests upon bluish mudstones, which at the adit are bleached to a pale tint; and the sandstone is followed by the oil-shale horizon, which is here of very inferior quality.

No signs of mineralisation are to be seen in the upper part of the sandstone, which is fully exposed, nor in the thick sandstone outcrops higher up the mountain-side; the molybdenum appears to be confined to the lowest 4 or 5 feet of sandstone and to a distance of outcrop of 20 yards at most—less than that if slight impregnation be disregarded. Along this face of rock the sandstone shows two irregular dark-stained areas, each a couple of yards across; an adit was driven in at this point to a distance of

about 200 feet, but the workings were ultimately abandoned. Prospecting had also been carried out with the aid of a diamond drill, boreholes being put into the hill-side at various angles to the horizontal; records of these are published in the Reports on the Mining Industry of Natal for 1906 and 1907. Only one of these cut the pebbly zone with which the molybdenum is associated; the rock was highly pyritic.

The exact boundaries of the deposit have not been determined, but the body appears to be irregular and small in size.

The ore on the dump is a peculiar friable black sandstone flecked with white, and carrying a fair amount of sulphide of iron; the latter is often very abundant in the form of spherical concretions from one to two inches across, and is mostly the mineral marcasite. Along one horizon they are crowded together, are about half an inch in diameter, and each concretion includes large numbers of quartz grains enclosed in the solid marcasite. Such concretions are present in fair number in the Indwe sandstone generally, but usually they have been oxidised and give rise at the outcrop to hollow, spherical, ferruginous masses.

The black sandstone is made up chiefly of dull rounded and sub-rounded grains of quartz, to which a black matter adheres that is insoluble in acids, and is principally carbonaceous in composition. Along certain bands in the sandstone the quartz grains are set in a minutely crystalline matrix, generally white, but occasionally a pale blue, due no doubt to the presence of molybdenum compounds. It is very soft, and was found to consist of minute plates of kaolinite derived from the alteration of the potash feldspar which is commonly a conspicuous constituent of the sandstone. More usually, though, by loss of the cementing material, the rock has been converted into a porous friable mass.

The sulphide of iron occurs as small crystalline aggregates; pyrite is certainly present, but, from the fact that some of the specimens show an efflorescence of sulphates, there must be marcasite as well.

The black amorphous matter surrounding the quartz grains is in great part, as already stated, carbonaceous, and as shown by the readiness with which it can be oxidised, cannot be graphite. It is insoluble in xylol, but with carbon disulphide or ether a small amount of hydrocarbon can be extracted which is not volatile, and the material is not unlikely to be of the nature of coal, streaks of which, it may be remarked, are not unusual in this sandstone. Lassaigne's test (with sodium), curiously enough, gave no reaction for nitrogen.

The molybdenum is associated with this black material, and can only be present in the form of the black sulphide, molybdenite, MoS_2 ; minute scales of this mineral were observed upon microscopic examination of the powder, and confirmation of this was obtained by the following analysis of a sample of the rock made by Mr. C. Garthausen in the laboratory of the Geological Survey:—

Silica	83.8 per cent.
Alumina	0.8 "
Sulphur	4.4 "
Iron	2.9 "
Molybdenum	1.1 "
Alkalis	Nil

Unfortunately, lack of the necessary apparatus prevented the determination of the proportion of carbon, but its value is obviously less than 6 per cent.

The sulphides are consequently present in the following proportions:—

Pyrite or marcasite ..	6.53 per cent.
Molybdenite	1.85 "

Most interesting are the oxidation products of the sulphide minerals in the rock. Some surfaces and joint planes are coated with a thin incrustation of bright yellow

molybdc ochre, a mineral which is not trioxide of molybdenum, as usually stated in text-books, but, as pointed out by Schaller (*Amer. Jour. Sci.*, 1907, xxiii., 297), a hydrous ferric molybdate, $\text{Fe}_2\text{O}_3 \cdot 3\text{MoO}_3 \cdot 7\frac{1}{2}\text{H}_2\text{O}$, formed by the oxidation of molybdenite in the presence of pyrite or marcasite.

Its identification was confirmed by chemical and optical tests.

In one case a bright lemon-yellow efflorescence formed on the specimen in the cabinet after collection in the form of small pin-points of a soft substance, which proved to be not molybdc ochre, but granular sulphur in part, originating most probably from the alteration of the molybdenite. On the same sample very small crystals of green ferrous sulphate had developed from the iron sulphide.

On the exposed face of sandstone there was a large patch of a thin incrustation which ranged in colour from nearly black to an intense prussian blue; the substance is soluble in water, and gives a strong reaction for molybdenum, and must, therefore, be the rare mineral *ilsemanite*, $\text{MoO}_2 \cdot 4\text{MoO}_3$, so far only known from Bleiberg, in Carinthia (W. Lindgren and F. L. Ransome, U.S. Geol. Surv., *Prof. Paper* 54, 1906, 124), as a product of decomposition of wulfenite, molybdate of lead, and from Cripple Creek, Colorado, as an alteration of molybdenite (E. S. Dana, "A System of Mineralogy," p. 202). In Natal, therefore, the mode of origin of this uncommon mineral is identical with that in Colorado.

The walls of the adit are coated with a friable yellowish incrustation which proved to be principally *aluminite*, a basic aluminium sulphate with a certain amount of iron, but devoid of lime, magnesia, or potash. A similar substance was found below the undercut base of the sandstone outcrop, where it was protected from the rain and is harder and more stalactitic in character and dull whitish in colour, with tints inclining from yellow-brown on the one hand to pale blue on the other; it is of interest because it contains a small amount of molybdenum, though how this is combined has not been ascertained.

As regards the genesis of the deposit, no definite suggestions can be made, unfortunately. As far as can be judged, the black molybdenum bearing part of the sandstone is irregular in shape, and in places fairly sharply defined from the rest of the rock.

The molybdenum compounds could not have been of detrital origin, for then the deposit would gradually fade away into barren sandstone on either side; also the quartz pebbles, when broken, are free from enclosed flakes of molybdenite. The presence of pyrite and marcasite is common indeed in the Indwe sandstone, but the amount present here is much higher than usual, and a great part of the sulphides of iron must therefore have been introduced later, probably along with the molybdenite.

Several such nodules from this sandstone at different localities in the Cape Province gave no indications of molybdenum when tested by the delicate reaction with stannous chloride.

The source of the carbonaceous matter is another difficult problem; its restriction to the ore-body will hardly allow of its being an original constituent, but on the other hand it is not volatile. In some ways it recalls the odd anthracitic "coals" found in irregular veins and fissures in the Western Karroo.

There are no signs of any channels up which ascending solutions could have made their way, and there are no dykes in close proximity. The only igneous intrusion is a nearly horizontal sill of dolerite, which crops out at a level fully 100 feet above the occurrence, and which might have been concerned in its genesis. This is not at all unlikely, for small amounts of iron and occasionally copper pyrites are found in these intrusions in the Karroo system; in the Insizwa range, in Mount Ayliff, there is a good deal of nickel as well (in the form of sulphide) along with pyrrhotite.

This sporadic occurrence of molybdenum in Natal may quite well be genetically connected with the intrusion of

the Karroo dolerites, but it is only fair to point out that prospecting has not brought to light any similar mineralisation at points a few miles away, where the sandstone has been cut through by the dolerite sheet in question.—*South African Journal of Science*, xiii., No. 4.

THE
PREPARATION OF HYDROCHLOROPLATINIC
ACID BY MEANS OF HYDROGEN PEROXIDE.

By PAUL RUDNICK and R. D. COOKE.

IN the preparation of hydrochloroplatinic acid, for use as a reagent in the determination of potassium or for other purposes, such as determinations of atomic weights of platinum and chlorine, many writers have emphasised the necessity for completely removing nitric acid and for completely oxidising the hydrochloroplatinic acid formed. (T. Knösel, *Ber.*, 1873, vi., 1159; G. Krause, *Zeit. Anal. Chem.*, 1875, xiv., 184; E. Dulliver, *Comptes Rendus*, 1877, lxxxiv., 444; H. Precht, *Zeit. Anal. Chem.*, 1879, xviii., 509; J. S. Stas, *CHEMICAL NEWS*, 1896, lxxiii., 5; H. W. Wiley, *Journ. Am. Chem. Soc.*, 1897, xix., 258; *CHEMICAL NEWS*, 1897, lxxv., 214). If the nitric acid is not completely removed by repeated evaporation with concentrated hydrochloric acid, nitrosoplatinic chloride, $\text{PtCl}_4(\text{NO})_2$, is formed, which eventually contaminates the product and compounds made from it. The directions usually given for the removal of nitrates seem to be somewhat vague and uncertain in their results. On the other hand, the solution in nitrohydrochloric acid and evaporation with hydrochloric acid results in the formation of hydrochloroplatinous acid, H_2PtCl_4 , which must be oxidised to hydrochloroplatinic acid, H_2PtCl_6 . This has always been accomplished, so far as the literature shows, by saturating the solution with chlorine and heating to expel the excess. The objection to the presence of either of these compounds is very well stated by J. W. Mellor, who says ("Quantitative Inorganic Analysis," 1913, 240):—

"Dissolve the grey powder at as low a temperature as possible in hydrochloric acid, and add nitric acid in small quantities at a time. In this way some nitrosoplatinic chloride, PtCl_4NO_2 , is formed. This must be destroyed, since it leads to low results in the determination of potassium. Evaporate the solution with water, whereby the nitrosoplatinic acid is decomposed into hydrochloroplatinic acid with evolution of nitrogen oxides. Some of the latter still remain in solution. Hence, add more water and hydrochloric acid and again evaporate. These operations are repeated until no more nitrous fumes are evolved. During these operations some hydrochloroplatinous acid is formed, H_2PtCl_4 . This is particularly objectionable, since it leads to high results when the chloroplatinic acid is used for the determination of potassium."

H. C. P. Weber, in preparing hydrochloroplatinic acid for the determination of the atomic weight of chlorine, dissolved the platinum by making it the anode of an electrolytic cell containing strong hydrochloric acid (*Journ. Am. Chem. Soc.*, 1908, xxx., 29; U.S. Bur. Stand., *Sci. Papers* 82, 1908). The solution had to be oxidised later by passing chlorine through it as described above. W. Dittmar and J. McArthur made hydrochloroplatinic acid for determining the atomic weight of platinum by dissolving platinum black in hydrochloric acid while passing chlorine into the solution, but they state that this was very tedious (*Trans. Roy. Soc. Edinburgh*, 1887, xxxiii., 561).

While these methods obviate the difficulty caused by the presence of nitric acid, they require expensive equipment or are so slow as to be prohibitive. The use of hydrogen peroxide in the form of a 30 per cent solution (perhydrol) had been suggested by one of us some years ago for completing the oxidation of the platonic chloride solution used in the determination of potassium, and has been success-

fully employed for this purpose ever since. Recently, the idea suggested itself to us that hydrogen peroxide might possibly replace nitric acid in the solution of platinum black in nitrohydrochloric acid, and on trial this proved to be correct. The addition of hydrogen peroxide readily effects the solution of platinum black in hydrochloric acid, yielding a solution of hydrochloroplatinic acid which is at once free from the nitroso compound and completely oxidised to H_2PtCl_6 . This reaction was briefly reported by T. Fairley in 1875 (*Brit. Assoc. Adv. Sci.*, 1875, xlv., 42; *Ber.*, 1875, viii., 1600), who is as briefly quoted by Gmelin-Kraut ("Handbuch der Anorganische Chemie," Part 3, vol. v., p. 170), but these inconspicuous statements seem to have escaped the attention of later writers. C. Marie (*Comptes Rendus*, 1908, cxlvi., 476) even reports that "hydrogen peroxide in acid or alkaline solution appears to be without action on platinum," but this is no doubt due to the fact that he operated on platinum-foil at ordinary temperature and not on platinum black. The reaction is apparently the result of a coincidence of three reactions. The catalytic influence of platinum black on the decomposition of hydrogen peroxide has long been known. With its oxidising power thus enhanced, the hydrogen peroxide oxidises the hydrochloric acid, liberating nascent chlorine, which in turn combines with the platinum.

The reagent for the precipitation of potassium may be prepared as follows:—Ten grms. of dried, but not ignited, platinum black are covered with 50 cc. of concentrated hydrochloric acid, warmed to about 50° or 60°, and 3 per cent hydrogen peroxide slowly added, keeping just enough present to maintain a moderate evolution of chlorine, which will be seen to originate entirely on the platinum. When the platinum has been entirely dissolved, evaporate the solution to a volume of 100 cc., when it is ready for use. The use of peroxide as dilute as 3 per cent may cause the volume to become too great during the operation. In this case it will be necessary to evaporate to a smaller bulk before the platinum has all been dissolved.

If "perhydrol" or concentrated hydrogen peroxide is available, it will be possible to keep the volume below 100 cc., thus shortening the time necessary to prepare the solution. The concentrated peroxide had best be added from a burette to avoid a large excess at one time, which might cause loss from frothing. We have found it convenient to prepare peroxide of 20–30 per cent strength by distilling commercial hydrogen peroxide under a pressure of 4–5 cm., and at a temperature of 35–45°. On concentration to one-eighth of the original volume, 80 per cent of the hydrogen peroxide remains in the residue, and the loss from decomposition is negligible.

We take this opportunity of acknowledging the assistance rendered by Mr. W. C. Beaumont in the work described in this paper.—*Journal of the American Chemical Society*, xxxix., No. 4.

RUSSIA AND BRITAIN.

AT the present juncture it is most unfortunate that our news service from Russia is so inadequate and one-sided. Probably it is inevitable in the circumstances; the newspaper correspondents are located in Petrograd, and the daily phases of political ferment loom much larger than the quiet unostentatious work going on behind the scenes. Unfortunately, such reports are those which have gained the chief currency out of Russia. For the time being Russia is the most free country in the world—there is no censorship, no ban on public meetings or free speech, scarcely any police to keep order. Imagine what would happen if a similar situation existed here. We should have Pacifist and Socialist demonstrations daily, while the people who were getting on with their work would be silent, and the country might easily be represented as mainly composed of stop-the-war fanatics. That is what is happening in Russia; and agitators, gorging on their

newly-won freedom, are letting off vast quantities of steam, which makes a lot of noise but is mainly quite harmless. It is perhaps just as well that the steam should be let off; at any rate it cannot be stopped at present.

But meantime we hear absolutely nothing except through private channels of the excellent work the Provisional Government has already accomplished. It has reorganised transport and supplies so effectively that food prices have fallen 200 to 300 per cent. In every village and township arrangements are being made to set up schools for elementary and technical education, which previously could only be done by the express sanction of the Central Government, with the result that in most cases it was not done at all. And preparations are on foot for establishing no fewer than forty-five technical universities, to which the poorest students will have access if they show the requisite ability. One of the most wonderful features of the Revolution is that almost its first—and certainly its most important—work has been the tackling of the education problem with a whole-hearted zeal that is quite amazing. Evidently the leaders of public opinion believe that a well educated proletariat is the surest and safest way to real progress.

It is very necessary that the British public should know these things, so as to form a just and proper opinion of what is happening. Liberated Russia looks more to Britain for help and guidance than to any other country, but we are, quite unwittingly no doubt, doing our best to nip the growing friendship in the bud. Already the tone of some of our newspaper articles has created first dismay and then a certain revulsion of feeling against us, and German agents are not backward in making the utmost use of the weapon we have placed in their hands. That is a truly deplorable state of affairs. After the war the development of Russia, with its population of 180,000,000, will provide almost unlimited trade openings, and it is of the utmost importance, in order that we may secure a proper share—it will be the lion's share—to treat the present troubles in a sympathetic and friendly spirit. That mistakes will be made before settled Government is firmly established must be expected, and fair criticism will be welcomed rather than otherwise, but at any rate it ought to be based on a broad and generous view of the situation as a whole, and not merely on the passing and less pleasing symptoms.—*Russo-British News Bureau, Ltd.*

“HOW TO MAKE ANIMALS TRANSPARENT!”

A CORRESPONDENT sends the following communication:—

How to render animals transparent was described recently in the Patents Court, which has been set up by emergency legislation to deal with the patents of alien enemies during the war.

The Trustees of the British Museum (South Kensington, Natural History Section) applied for licence to use the German patent 8621 of 1909, in the name of Streller, which provides a process “for rendering organic and inorganic bodies transparent and translucent,” by the employment of the refraction of light.

Explaining the process, Dr. S. F. Harmer, F.R.S. (from the Natural History Museum), said it undoubtedly was a remarkable one. It offered peculiar advantages for the study of the internal structure of animals. One could take, he said, a rat, and prepare it in a certain way, put it in certain solutions specified, and it would become extremely transparent, so that one could see the details of the skeleton through the skin and muscles. They desired to make use of the process at the South Kensington Museum. The general principle of making objects transparent by putting them in liquids of suitable refracting indices they knew before the patent, and the patentee could not claim any patent rights in general scientific principles. Formulae for various solutions under the patent were set forward in

a German book he had in his hand, by Dr. Spalteholz, published in Leipzig in 1914. The professor described details of various processes, and the authorities desired to employ most of them. The particular details of some of these processes were new. The Museum wished to use them partly for preparing objects to be exhibited to the public and partly for study purposes. He was not sure that all the chemical substances could be obtained in this country at the present time. Some of them were complicated bodies which were made in Germany. The processes were probably capable of use for commercial as well as scientific purposes. If, for instance, a farmer had a sample of seed, and he wished to examine the quality of the seed, or see whether it was internally attacked by insects or disease, it was quite possible that the seed should be made transparent in this way, and it would be a convenient mode of judging of its goodness or otherwise. Turning to the specifications, the patentee states the principle in this way: An object with a certain index of refraction attains the property of transparency if placed in a liquid having a corresponding index of refraction. If a particular tissue or constituent is to be examined, the index of refraction of the solution must have particular reference to the index of refraction of that particular organic constituent. Or, with many constituents in the body, the index of refraction of the liquid may correspond to the mean of these indices. In the patentee's words: “Supposing that it is animal bodies which are to be rendered transparent, they will be as completely saturated as possible with a liquid the index of refraction of which corresponds either to the mean of the indices of refraction of the different tissue constituents of the particular bodies or to the index of refraction of one of these constituents in a dry state. The index of refraction of this body or of its parts may be determined in any of the known methods, and the liquid chosen or composed to correspond to this index of refraction. An example of such a liquid, the index of refraction of which corresponds to most of the animal tissues, is a mixture of three parts of salicylic methyl ester and one part of benzyl-benzoate.” Water is often present in high percentage. The human cardiac muscle contains 80 per cent.

Bodies need to be prepared in certain ways, such as by having gases, air, or water removed by an air-pump, so that the saturation takes place in a vacuum. For the removal of water, a preliminary treatment of the body with alcohol, benzol, or the like, may be carried out.

In some cases, liquids may be chosen which, by virtue of their index of refraction, cause certain parts or groups of the body to disappear, so to speak, and thereby bring other parts the more prominently into view.

Dr. Harmer added that Prof. Spalteholz, in his book, stated that a licence must be obtained by the purely commercial use of the patent; but its employment for scientific preparation and educational purposes was in another case. The purely scientific use of the process remained free.

The Controller of Patents (Mr. Temple Franks) said this almost seemed to obviate the necessity for a licence. There was also the question whether the patent was good, since it seemed to endeavour to patent the use of general scientific principles. There was the further fact that this was wanted for a Government and public institution. He would look into the matter.

Camphor.—The production of camphor in Japan for the year ending March 31, 1917, is estimated at 1,627,422 kin (a kin is 13 lb.), an increase of 26,607 kin as compared with the yield in 1915-16, while the estimated production in Formosa amounts to 5,014,743 kin, an increase of 394,561 kin, as compared with the yield in the preceding year. The production of camphor oil in Japan for 1916-17 is estimated at 3,210,494 kin, an increase of 209,073 kin as compared with the yield in 1915-16; the estimated production in Formosa is 7,827,560 kin, or 946,328 kin in excess of the yield in 1915-16.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, May 17, 1917.

Sir J. J. THOMSON, O.M., President, in the Chair.

THE Bakerian Lecture was delivered by Mr. J. H. JEANS, F.R.S., on "*The Configurations of Astronomical Masses and the Figure of the Earth.*"

A study of the forms which can be assumed by masses of actual compressible matter under their own gravitation is of obvious importance for cosmogony and astronomy. A theorem of fundamental importance is that for a given mass, acted on by given forces and rotating at a given speed, there is only one equilibrium arrangement of the internal strata when the boundary is fixed. Thus possible figures of equilibrium can be classified by their boundaries; the interior matter will arrange itself.

A simple application is to the Figure of the Earth. Regarding the earth's surface as roughly spherical, the internal layers of equal density must be concentric spheres. The view that the internal strata may be, or in some past age may have been, excentric, is found to be illusory, and an attempted explanation of the major inequalities of the earth's surface in terms of this idea fails.

A more complex application is to the figures of compressible masses, such as gases, in rotation. It is found that a shrinking compressible mass will, in general, assume in turn figures which may be described as pseudo-spheroids and pseudo-ellipsoids, these being derived by continuous distortion from the spheroids and ellipsoids which form the only stable figures of equilibrium for incompressible masses. The pseudo-spheroids are more lens-shaped than a spheroid, and the pseudo-ellipsoids are more spindle-shaped than an ellipsoid. A sharp periphery may develop on the pseudo spheroid or a sharp point on the pseudo-ellipsoid, in which case streams of matter are ejected through centrifugal force outbalancing gravity.

Considering in detail the figures appropriate to the law $p = \kappa \rho \gamma$, it is found that a sharp periphery will develop on the pseudo-spheroids before the series of pseudo-ellipsoids is reached if $\gamma < 3$ (approximately). Thus a mass of ideal gas for which $\gamma < \frac{5}{3}$ can never attain the pseudo-ellipsoidal form, and so can never divide into two detached masses. But as the density of an actual gas increases with shrinkage, the ideal laws are departed from. The value $\gamma = 3$ is reached, perhaps, at a density of $\frac{1}{4}$ to $\frac{1}{2}$, roughly that of a B-type star. So far, then, a "giant" star can lose matter equatorially, but cannot divide by fission. The latter process can only begin at about type B. This agrees exactly with Campbell's discussion of spectroscopic binaries.

In an actual star internal ionisation and pressure of radiation must be considered, so that a star of sufficient mass can break up before B-type is reached, and there can be "giant" double stars.

The results obtained fit in well with observation, and suggest a simple view of stellar cosmogony.

FARADAY SOCIETY.

Ordinary Meeting, May 1, 1917.

Sir OLIVER LODGE, F.R.S., in the Chair.

A GENERAL DISCUSSION took place on "*Osmotic Pressure.*"

Sir ROBERT HADFIELD, F.R.S., President, in opening the proceedings, said he only did so in order to introduce Sir Oliver Lodge to the chair. Speaking as a metallurgist, he hoped that consideration of the subject under discussion would be found to have some bearing on the scientific problems of ferrous metallurgy, such as the solution of carbon in iron.

Sir OLIVER LODGE then took the chair.

Sir Oliver referred in the first instance to the general importance of the subject in animal and vegetable economy. That was the practical side; but the discussion was to concern itself with the theoretical side. Osmosis depended essentially on molecular discrimination, and this brought it into relation with evaporation and freezing. The subject could be treated either thermodynamically—disregarding what actually goes on—or from the kinetic standpoint, and that was how the authors of the papers would treat it: Dr. Porter applying the gas theory to the dissolved substance, Mr. Bousfield to the solvent, and Dr. Tinker dealing with the matter on a cohesion basis.

Prof. ALFRED W. PORTER, F.R.S., then opened the discussion by the presentation of his paper.

The investigations of Perrin and others upon Brownian motion have demonstrated once for all that the molecular translatory agitation in a liquid is precisely that which is given by gas theory. This had long been suspected but never proved. In considering a solute the dynamical effects of this motion must be taken into account; when the solution is dilute it comes out equal to the experimental value of osmotic pressure. Any other theory of osmosis must not only explain it, but at the same time must explain away the effects of molecular agitation. Of course, when the processes by which the final equilibrium state is set up, or the properties of the membrane which make it semi-permeable, come to be examined, many interesting connections will certainly be found which will make it possible to express osmotic pressure in terms of them; but the *causa causans* of the whole phenomenon is the molecular bombardment of the solute, and a knowledge of this provides us with the *only way* in which the value of the pressure has been calculated from any direct theory of the mechanics of the solution. The properties of the membrane form a subsidiary problem; they have as much to do with osmosis as the properties of a glass vessel have upon the origin of the pressure experienced from water contained in it.

The experimental values of Lord Berkeley and Morse and their co-workers for sugar solutions can be approximately represented by a formula of Hirn's type, $P(v-b) = RT$; but the values of b are larger than the volume occupied by the sugar itself. The excess can be attributed to water of hydration. The hydration number found in this way from Morse's determinations diminishes with increase in temperature, and also with increase in concentration. The extreme values are 53 and about 3. The value 53 occurs only in a very dilute solution, and the corresponding value obtained from Berkeley's experiments is only 14, which seems a more likely number. If the molecules of sugar and water are represented by spheres of volumes equal to their molecular volumes, between 30 and 45 molecules of water would form a single layer on each sugar molecule. It is exceedingly likely *a priori* that the water round a sugar molecule tends to form a condensed layer on it which will be continually breaking up under the influence of molecular collisions. There is nothing in osmosis to indicate the degree of association of water molecules with each other; mono-, di-, tri-hydrol are indistinguishable.

Doubt is thrown upon the meaning of the symbol N in Poynting's and Callendar's modifications of Raoult's equation. Their theories require that N shall be the total number of real molecules of solvent, whereas thermodynamical theory and experiment require that it shall be the number reckoned as of the same complexity as in the vapour state.

Osmotic pressures can be obtained indirectly from vapour pressures by an exact relation first given by the opener; this has been done experimentally by Lord Berkeley. They can also be obtained from latent heats of dilution either by an exact formula given by the opener or by a better-known approximate formula:—

$$H_i = uT^2 \frac{\partial}{\partial T} \left(\frac{P}{T} \right).$$

Values of H_i are being determined by D. O. Wood; some of these are published now for the first time, and Morse's determinations are checked by them. This mode of indirect determination of osmotic data is very exact because H depends only upon deviations of P from the perfect gas law, being zero when P is proportional to T .

Dr. F. TINKER then presented his paper on "*The Colloidal Membrane: Its Properties and its Function in the Osmotic System.*"

In this contribution the kinetic side of the subject of osmosis is developed by the aid of data obtained from the experimental study of colloidal membranes. Evidence is brought forward to show that moisture flowing through a semipermeable membrane is absorbed or superficially condensed on to the surfaces of the colloidal particles composing the film for such time as it is in contact with the membrane.

Generally speaking, osmotic flow takes place from a pure solvent to a solution because the pure solvent induces a greater pressure of concentration of moisture inside the membrane than the solution does. The condition for osmotic equilibrium is uniformity of moisture pressure and concentration within the membrane. To establish this uniformity, a hydrostatic pressure has usually to be placed on the solution in order to bring the moisture pressure generated by it inside the membrane up to that generated by the pure solvent. The particular hydrostatic pressure which does this is defined as the osmotic pressure of solution.

The evidence adduced points to the conclusion that osmotic diffusion is a process similar in character to, but *not* identical with, the process of vapour distillation. The main difference between the two processes is that the moisture within a membrane is in a much more concentrated condition than it is inside the vapour phase proper. But the resemblance is so great that for purposes of argument and mathematical treatment we can replace the actual membrane by a vacuum; at least this is the case when considering quantities, such as the magnitude of the osmotic pressure, whose value is independent of the nature of the membrane. By means of this simple device the process of vapour distillation becomes a particular type of osmotic diffusion, viz., osmotic diffusion across a vacuum. We can consequently arrive at many of the factors governing the magnitude and direction of osmotic flow, and the magnitude of the osmotic pressure, by considering the factors which determine the relative values of the vapour pressures of the pure solvent and solution respectively. This is done in the latter part of the paper.

Mr. W. R. BOUSFIELD, K.C., F.R.S., then gave his paper entitled "*Osmotic Pressure in Relation to the Constitution of Water and the Hydrates of the Solutes.*"

This paper deals with the subject of osmotic pressure from the standpoint of the ternary constitution of water, which alone can explain the curious fact that for a very dilute solution of sugar the osmotic pressure at 0°C . is greater than that at 5° . The vapour pressure theory is shown to be sufficient to explain all the phenomena without postulating osmotic pressure as an "expansive force."

It is shown that the osmotic relationships can be deduced with great accuracy on the simple hypothesis that the steam molecules in water behave as a perfect gas in the interstices of the solution. The conclusion is that it is not the solute but the interstitial vapour of the solvent which behaves as a gas, and that it is not the activity of the solute but that of the solvent vapour which is responsible for the phenomena.

Mr. W. R. BOUSFIELD proceeded to discuss the views put forward by Prof. Porter. A theory which left out of account, comparatively speaking, the activity of the solvent, seemed to him the wrong way of looking at things. Criticising the contention that the diffusion, say, of sugar introduced into a solution indicates an expansive force, he maintained that osmosis might be equally regarded as due to the water expanding in the opposite direction. If the

pressure of sugar arose from its thermal motion, why at the surface was it the vapour of the water which escaped and not the sugar? What really obeyed the gas law in solution was not the solute but the occluded vapour comprised in the solution. Figures calculated from his theory agreed with those observed more closely than those deduced from Prof. Porter's theory.

Dr. S. A. SHORTER held that the "gas law" of osmotic pressure, though simple from an algebraical point of view, was very complex from the point of view of the kinetic theory, so that the law formed a very unsatisfactory basis for the theory of the ideal dilute solution. The correct basis for the theory was Henry's law, which stated that the partial pressure of the solute was proportional to its concentration, and which was readily established on theoretical grounds—simply following from the obvious consideration that the field of force, in which each solute molecule moved, was not affected by the addition of further solute molecules. The constant of proportionality depended upon the nature of the intermolecular forces, being vastly greater in the case of, say, solutions of benzene in water, than in the case of, say, solutions of methyl alcohol in water. From Henry's law we could readily establish Raoult's law and the "gas law" of osmotic pressure, neither of which could be deduced from simple theoretical considerations, and neither of which contained any reference to intermolecular forces. This latter point constituted a grave defect in the ordinary osmotic theory. Since it ignored intermolecular forces in dilute solutions, it led many investigators to ignore them in concentrated solutions, and to adopt the totally unjustifiable procedure of postulating certain ideal properties of a concentrated solution, and then ascribing departures from this ideal to chemical action (dissociation, association, or solvation). Now, it was evident, from a consideration of the theoretical basis of Henry's law, that intermolecular forces must control the mode of variation with concentration of the partial pressure of the solute in a concentrated solution. The same must be true of the partial pressure of the solvent, and of the osmotic pressure, since they were both related thermo-dynamically to the partial pressure of the solute. Theories of the chemical structure of concentrated solutions, based on the concept of the ideal concentrated solution, were fundamentally unsound.

The most necessary step towards a fuller knowledge of the processes operative in solutions was the further development of the kinetic theory of solution. The points to be explained first of all were not the comparatively minute deviations from some imaginary ideal behaviour exhibited by certain solutions, but such broad questions as the existence of different types of partial vapour pressure curves, the total or partial miscibility of liquids, the existence of a critical temperature with respect to miscibility, &c.

The EARL OF BERKELEY, F.R.S., as an illustration of one of the difficulties in the internal vapour pressure theory, referred to the diffusion which would take place if a layer of potassium bichromate were placed at the bottom of a column of concentrated sulphuric acid, the vapour pressure of which was practically nil. He inquired as to the accuracy of the latent-heat method of measuring osmotic pressure.

Prof. J. C. PHILIP stated difficulties he felt with regard to Dr. Tinker's explanation of the selective action of the membrane. As far as size was concerned, a sugar molecule could pass through the pores of the membrane. If the pores had the power of absorbing water, why should not that water absorbed itself take up the sugar molecules making the membrane "leak"? Recent experimental work on hydration led to somewhat higher figures for the average number of water molecules associated with sugar in solution than the numbers assumed by Mr. Bousfield, namely, from 11 in dilute down to about 7 in strong solutions. Prof. Porter had obtained similarly higher figures.

Dr. G. SENTER, while agreeing largely with Prof.

Porter's theory, criticised his views on hydration, and in particular the assumption that the uncertainty in the value of b in Hirm's equation was to be accounted for by hydration.

Mr. W. C. DAMPIER WHETHAM, F.R.S., was of opinion that the relations between osmotic phenomena and vapour pressure and freezing-point which Mr. Bousfield had deduced amounted in effect merely to a confirmation of thermodynamic relations. To get a satisfactory theory of the mechanism of osmotic pressure it was necessary to begin with first principles, and he thought the gas theory the only one which enabled this to be done.

Prof. A. FINDLAY, in a written communication, emphasised the importance of distinguishing between the equilibrium pressure and the process by which this was produced. The process of osmosis and the role of the membrane had little reference to the main problem of the value of the equilibrium pressure and its relation to the constitution of the solution. He combated the view that osmotic pressure (a term he thought misleading) was to be identified with the expansive force that brought about diffusion, and he could not accept Prof. Porter's kinetic treatment of the problem. The weakness in this arose from the use of the equation $P(v-b) = RT$ in attributing deviations from it to hydration. The connection between heat of dilution and osmotic pressure seemed a fruitful direction for investigation. He favoured the view, mooted by Tammann, that osmotic pressure was caused by the inner compression of the solvent in solution. Some recent calculations by Horiba lent support to this theory.

Mr. J. R. PARTINGTON, in a written communication, showed how it followed from molecular theory that although the physical state of the dissolved molecules might not be comparable with that of the gaseous molecules, yet they could behave with respect to bombardment as if they were in the state of a gas. The question as to whether the osmotic pressure was "caused" by solute or solvent appeared to him to be largely meaningless.

Mr. F. S. SPIERS (communicated) considered that a satisfactory conception of osmotic pressure was arrived at if one regarded it as the *diminution* in the kinetic molecular energy of the solvent due to association with the solute. This view not only took account of both solvent and solute, but it also gave a simple picture of the process of osmosis, and suggested at once the connection between osmotic pressure and vapour pressure.

Prof. ALFRED W. PORTER replied at this stage to some of the criticisms that had been made. The solute molecules contribute nothing to vapour pressure, simply because when they get near the surface they are drawn downward by the solvent and never succeed in escaping. The answer to Dr. Philip was, he thought, that the canals in the membrane must be narrow compared with the range of molecular action, although not necessarily compared with molecular dimensions. In answer to Lord Berkeley, the method of using latent heat of dilution to determine osmotic pressures gave very considerable accuracy. He reserved his full reply for the printed report of the discussion.

Prof. T. S. MOORE considered that the modification of the gas theory required to explain the action of a solute in solution was so fundamental that it ceased to be a gas theory. The internal pressure of a solution being exceedingly high, it was impossible to suppose that the pressure exercised by the solute molecules could be independent of the solvent molecules and of the forces exerted by the solute on the solvent, which were the assumptions made by Prof. Porter. A molecular theory of osmotic pressure must form part of a general molecular theory of solution.

Sir OLIVER LODGE, in bringing the discussion to a close, pointed out that in a liquid they had to deal with an internal pressure, due to the mutual attraction of the molecules, of great magnitude. The source of osmotic pressure was probably to be looked for in this internal pressure.

NOTICES OF BOOKS.

Industrial and Manufacturing Chemistry. Part II. Inorganic. By GEOFFREY MARTIN, Ph.D., D.Sc., F.C.S. Volume I. London: Crosby Lockwood and Son. 1917. Pp. xix+496. Price 25s. net.

THIS book is the companion volume to the author's "Treatise on Industrial Organic Chemistry," and is very similar to it in scope and plan. The impossibility of treating adequately the whole of industrial inorganic chemistry, even in two large volumes, is obvious, and although the editor has, on the whole, apportioned out his space wisely and has benefitted by the co-operation of a representative set of able collaborators, the descriptions of the technical processes are in some cases necessarily rather meagre. An enormously wide field is covered in the 51 sections which comprise the book, including fuels, gases, acids, salts, the liquefaction of gases, pyrometry, the technology of water, &c., and much attention has been paid to patent literature, and to modern processes and plant, details of which are in some cases published for the first time in book form. Diagrams and illustrations are very numerous, and the references to literature are full and detailed. The value of the book would probably be greater to technical students and to practical business men who want a survey of a good many branches of industrial chemistry than to the specialist in any one branch.

Chemistry for Beginners. By C. T. KINGZETT, F.I.C., F.C.S. London: Baillière, Tindall, and Cox. 1917. Pp. vi+106. Price 2s. 6d. net.

THE advisability of giving some simple scientific instruction to all children is in process of being recognised by educational authorities and parents, and it is most desirable that any distinction in this respect between the children of the rich and the poor should be reduced to a minimum. Any book therefore which is intended, as this, for use in primary and public schools should be assured of attention and welcome, if it appears satisfactory for its purpose. Physics and chemistry ought certainly to take very important places among the sciences, if they are not given precedence of all others in the school curriculum. The obvious criticism to be made with reference to this book is that its price is heavy for its scope and size. In addition, although it contains a very fair amount of information, it appears rather doubtful whether the material is put before the pupil in such a way as to make him use his reasoning power. The first part deals with the constitution of matter and the elements of the atomic theory, and would probably be found a rather difficult beginning for the average boy or girl. Part II. on "Force and Energy" is, on the whole, more likely to prove interesting, but the third part, in which short descriptions are given of the chief elements and compounds, is packed much too full of facts which will stand very little chance of being properly assimilated. Nevertheless, for the general reader who is interested in chemistry, the book will provide a useful review of the chief facts and will possibly help in the spreading of scientific knowledge in this country.

Guide to the Registration of Business Names Act, 1916. By KENNETH BROWN. London: Sir Isaac Pitman and Sons, Ltd. Pp. vii+51. Price 1s. net.

THIS little book gives in clear and unequivocal language precise information as to the provisions of the Registration of Business Names Act. Details of the circumstances in which registration is obligatory, the particulars which have to be furnished on registration, and the penalties attached to failure to comply with the Act are stated so plainly that it would appear to be impossible for anybody to misunderstand them. Many difficult and obscure points are fully discussed, and the full text of the Act is included, and

business men will find that the book gives clear and concise guidance on questions relating to the registration of business names.

The Journal of the Institute of Metals. Volume XVI. Edited by G. SHAW SCOTT, M.Sc. London: The Institute of Metals. 1916. Pp. ix+370.

THIS volume of the *Journal of the Institute of Metals* contains the 1916 May Lecture, delivered by Prof. W. H. Bragg on "X-Rays and Crystal Structure, with Special Reference to Certain Metals." The work of Prof. Bragg and others on the structure of crystalline materials may truly be described as laying the foundations of a new science, and undoubtedly results of the most far-reaching importance are awaiting investigators who employ the new methods of research which Prof. Bragg and his son have elaborated. Although it was not possible in the lecture to give more than a sketch of the work on X-rays and crystalline structure this was done in a very interesting and illuminating manner. Three papers on the annealing of arsenical brass, the allotropy of silver, and the development of the spelter industry, with accounts of the discussions which followed them, form the bulk of the book, which also contains short abstracts of papers on metals and metallurgy published in various English and other journals during 1916.

Dominion of Canada, Department of Agriculture. Report of the Division of Chemistry. By FRANK T. SHUTT, M.A., D.Sc. Ottawa: J. de L. Taché. 1916.

In this report of the work of the year 1915-1916 the Dominion chemist, Dr. F. T. Shutt, announces that some of the research work of the Division of Chemistry has had to be abandoned owing to the absence on active service of some of the members of the staff, and the impossibility of getting sufficient skilled assistance to continue all the work contemplated or begun. At the same time owing to the greatly increased demands for analyses from farmers and others, the routine work has become considerably heavier than before. Many analyses of feeding-stuffs are given in the report with some general conclusions; for example, as to the relative value of different kinds of roots and of different varieties of the same root, and a very interesting series of experiments on fertilisers has been carried out. Some calculations of profit and loss have been based upon the results obtained, and a considerable amount of useful information has been brought to light in the general discussion of these results.

MEETINGS FOR THE WEEK.

MONDAY, 4th.—Royal Institution, 5. (General Meeting).

— Society of Chemical Industry, 8. "Utilisation of the Sulphur contained in Zinc Ore," by H. M. Ridge. "Rate of Reversion of Mixtures of Superphosphate with Basic Slag and Rock Phosphates," by G. S. Robertson. "Some Observations on Crude (Coke Oven) Benzoles," by P. E. Spielmann and G. C. Petrie.

TUESDAY, 5th.—Royal Institution, 3. "The Flow of Ice and of Rock—The Flow of Rock," by Prof. W. W. Watts, F.R.S.

— Röntgen Society, 8.15. (Annual General Meeting). Adjourned Discussion on "The Future of the British X-Ray Industry."

WEDNESDAY, 6th.—Society of Public Analysts, 8. "Some Experiences in the Use of Copper Sulphate in the Destruction of Algae," by G. Embrey. "Combined Reichert-Polenske and Modified Shrewsbury-Knapp Process" and "Differentiation between Coconut and Palm Kernel Oils in Mixtures," by G. D. Elsdon. "Orange-pip Oil," by Dorothy G. Hewer. "Estimation of Theobromine," by Norah Elliott and G. Brewer. "Rapid Estimation of the Strength of Sulphuric Acid," by H. Droop Richmond and J. E. Merryweather.

THURSDAY, 7th.—Royal Institution, 3. "The Art of the Biographer," By A. C. Benson, C.V.O.

FRIDAY, 8th.—Royal Institution, 5.30. "Industrial Applications of Electrons," by Prof. Sir J. J. Thomson, O.M.

SATURDAY, 9th.—Royal Institution, 3. "The Electrical Properties of Gases," by Prof. Sir J. J. Thomson, O.M.

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THE CHEMICAL NEWS

Vol. CXV., No. 3002.

VOLUMETRIC DETERMINATION OF SULPHUR IN PYRITES.

By T. J. I. CRAIG, D.Sc.

(Concluded from p. 255).

Experimental Investigations.

FOR use in the following experiments a set of volumetric apparatus was provided, each vessel being carefully tested and regraduated where necessary.

I. *Elimination of Nitric Acid.*—It is well known that nitric acid can be completely removed from aqua regia solution of pyrites by taking to dryness once or twice, after adding strong hydrochloric acid. This is always done in the gravimetric determination of the sulphur as BaSO_4 . The same means were adopted to render the aqua regia solution free from nitric acid preliminary to carrying out the volumetric determination by titration with standard alkali.

To obtain a solution which would provide a number of experimental portions, 20 grms. of pyrites, ground to pass through a 100-mesh to the inch sieve, were dissolved in 600 cc. of aqua regia ($3\text{HNO}_3:1\text{HCl}$), evaporated to dryness overnight, treated with strong HCl , again taken to dryness, heated at 110°C . for one hour, dissolved in cold distilled water, filtered, and washed into a 500 cc. flask, and made up to the mark (each 25 cc. = 1 grm. pyrites).

The method of Pelouze was employed to determine the nitric acid, if any, in the solution (*Journ. Prakt. Chem.*, xl., 34).

Standard solutions were made of $\text{N}/10\text{KMnO}_4$ and FeSO_4 , such that 2 grms. of the latter were equivalent to 4.575 cc. of the former—the standardisation being carried out under the same conditions as in the test. 25 cc. of the above pyrites solution were boiled with 2 grms. FeSO_4 solution, 10 cc. HCl , and 25 cc. water down to half the bulk of the mixture. On cooling and titrating with the permanganate 4.55 cc. were used. In another experiment carried out in the same way, 4.6 cc. KMnO_4 were used.

The average of these two trials is 4.575, which is exactly the amount for 2 grms. of the FeSO_4 solution, thus proving absence of nitric acid.

Removal of Nitric Acid from the Dilute Nitric Acid and Bromine Method of Dissolving Pyrites.—Five grms. of pyrites (ground to pass through 100-mesh per inch sieve) were treated in a covered 800 cc. beaker with a mixture of 50 cc. strong HNO_3 , 1.42 sp. gr., and 50 cc. distilled water. An action with generation of much heat at once set in, and continued until all the pyrites was decomposed and dissolved with the exception of a small amount of sulphur. On cooling to 50°C . and adding 3 cc. bromine, and shaking gently round, the bromine gathered up all the sulphur. A further 20 cc. of strong nitric acid were now added, and the vessel and contents were warmed up on the steam-bath, and finally boiled on a flame for a few minutes. All the sulphur was oxidised and dissolved. The solution was now transferred to a porcelain basin and taken to dryness on the steam, moistened with water, and dried again, and finally heated in the air-bath for one hour at 110°C . About 50 cc. of distilled water were then added and heating on the steam applied for half-an-hour to thoroughly hydrate and dissolve the residue. The solution was cooled, treated with another 50 cc. of cold distilled water, stirred for a few

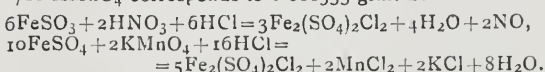
minutes, and filtered into a 250 cc. flask. The insoluble matter was washed with cold distilled water till acid free. The filtrate and washes were then made up to 250 cc., and well mixed. Each 50 cc. represents 1 grm. of pyrites. The method of Pelouze was again employed to determine the nitric acid, if any, in this solution. 50 cc. were treated in a 200 cc. flask with 10 cc. strong HCl , 1.16 sp. gr., and 10 cc. of a standard (approximately $\text{N}/10$) solution of FeSO_4 boiled for five minutes, cooled, diluted to about 500 cc., and the remaining FeSO_4 determined by titration with $\text{N}/10\text{KMnO}_4$. The FeSO_4 solution was standardised by taking 10 cc. of it, adding 50 cc. distilled water, 10 cc. strong HCl , boiling for five minutes, cooling, diluting to 500 cc. and titrating with $\text{N}/10\text{KMnO}_4$.

By carrying out the analytical test and the standardisation under the same conditions, any disturbing influence will be practically the same in each case, and will therefore not materially affect the result.

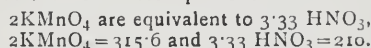
The FeSO_4 solution keeps very well if it is slightly acidified with H_2SO_4 , and a few strips of metallic aluminium are immersed in it.

It was found in the blank experiment that 10 cc. of the FeSO_4 solution were equal to 9.9 cc. $\text{N}/10\text{KMnO}_4$. In the analytical test for HNO_3 10 cc. of the FeSO_4 solution also used 9.9 cc. of the $\text{N}/10\text{KMnO}_4$, thus showing the absence of HNO_3 . A repetition of this experiment gave a similar result.

As it takes some considerable time to thoroughly dry the pyrites solution on the water-bath, it will be found quite suitable when a quick result is desired, to take the dried residue as soon as it ceases to give off visible fumes of HNO_3 and proceed with the solution and filtration of it. The small amount of HNO_3 remaining in the solution may then be easily determined and allowed for; each cc. $\text{N}/10\text{KMnO}_4$ corresponds to 0.000533 grm. S.



It is obvious from these equations that—



One cc. $\text{N}/10\text{KMnO}_4$ contains 0.003156 grm. KMnO_4 . Therefore—

1 cc. $\text{N}/10\text{KMnO}_4$ is equivalent to 0.0021 grm. HNO_3 ,
2 HNO_3 are equivalent to $\text{S} + 2\text{HNO}_3 + \text{S} = \text{H}_2\text{O} + 2\text{NO} + \text{SO}_3$,
126 grms. HNO_3 are equivalent to 32 grms. S.

Therefore—

0.0021 HNO_3 corresponds to 0.000533 grm. S;
that is—

each cc. $\text{N}/10\text{KMnO}_4$ corresponds to 0.000533 grm. S.

II. *Experiments on Removal of HCl from Aqua regia Solution of Pyrites.*—The HCl remaining in the first pyrites solution described under I. was determined by taking 25 cc., treating with 2 grms. pure CaCO_3 , heating on the steam, filtering and washing on the pump. 15.95 cc. of $\text{N}/10$ silver nitrate solution were used. This is equivalent 1.595 cc. of $\text{N}/1$ alkali.

25 cc. pyrites solution evaporated to dryness and the Cl determined as above described took 13.4 cc. $\text{N}/10\text{AgNO}_3$.

25 cc. dried, taken up with 10 cc. distilled H_2O , and dried again, took 11.45 cc. $\text{N}/10\text{AgNO}_3$.

25 cc. dried, dissolved in 10 cc. distilled H_2O , dried again, then once more treated with 10 cc. distilled water and dried, used 9.65 cc. $\text{N}/10\text{AgNO}_3$.

25 cc. treated with 10 cc. $\text{N}/1\text{H}_2\text{SO}_4$ and taken to dryness used 1 cc. $\text{N}/10\text{AgNO}_3$.

25 cc. treated with 5 cc. strong nitric acid and dried on the steam-bath took 6.05 cc. $\text{N}/10\text{AgNO}_3$.

25 cc. pyrites solution treated with 5 cc. strong nitric acid, dried, and heated at 110°C . in the air-oven for three-quarters of an hour took 0.6 cc. $\text{N}/10\text{AgNO}_3$.

It is obvious from these experiments that it is difficult to eliminate HCl by evaporation from the pyrites solution.

The best plan therefore is to bring the HCl as low as possible by the evaporation at the end of the aqua regia attack when removing the nitric acid. It may then be determined as already described and subsequently allowed for. Or, alternatively, the remaining HCl may be removed from the pyrites solution by means of a slight excess of pure moist silver oxide in the cold. The precipitate of silver chloride along with some unacted on silver oxide is of a dense nature, easy to filter off and wash. If desired, the silver chloride precipitates may be preserved and silver oxide recovered for re-use by a treatment with hot caustic potash solution, filtering and washing free from alkali and chlorine. Silver oxide removes all the HCl, and the precipitate of AgCl was proved to be free from sulphate by treating it with pure boiling caustic potash, filtering, acidifying with HCl, and adding BaCl₂. No trace of BaSO₄ was produced.

III. *Investigations Regarding the Arsenic.*—Experiments were made with the solution of pyrites hereinbefore described. This solution was made from a pyrites containing 0.02 per cent As, which is fairly low. In order to study also the behaviour of the arsenic when testing an arsenical pyrites, arsenic acid was added to the portion taken for analysis to bring up the arsenic to 0.5 per cent As on the pyrites.

25 cc. pyrites solution were diluted with 300 cc. distilled water in a porcelain basin, a little phenolphthalein solution

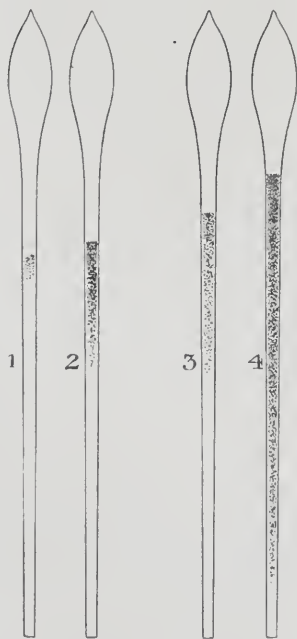


FIG. 1.

- 1 (filtrate) and 2 (precipitate) show, by comparison, that in a pyrites containing 0.02 per cent arsenic practically all the arsenic goes down in the precipitate.
3 (filtrate) and 4 (precipitate) from a pyrites containing 0.5 per cent arsenic. The most of the arsenic is in the precipitate.

was added, and then standard alkali until a permanent red colour was produced in the liquid. 4 cc. additional alkali were then added, and the liquid was brought to the boil. After boiling for about a minute the whole was transferred to a 500 cc. flask, cooled to the room temperature, and made up to the mark.

The precipitate of ferric hydrate was filtered off, washed, dissolved in arsenic free H₂SO₄, and the solution made up to 100 cc. The filtrate was preserved without the washings.

Aliquot portions (one-tenth) of the precipitate solution and of the filtrate were each tested for arsenic in the manner recommended by the Committee for the purpose of ascertaining the best method for determining small quantities of arsenic, and described in the *Journ. Soc. Chem. Ind.* (xxi., 94).

Two further tests were made similar to the last one, but with the addition of arsenic acid to the pyrites solution to bring the amount of arsenic in each group up to 0.0005 gm. As per gm. of pyrites (i.e., 0.5 per cent on the pyrites).

The results of these experiments are seen in the photograph (Fig. 1) of the arsenic deposits, and it is clearly shown that practically all the arsenic is removed from the solution by the precipitated ferric hydrate, and does not therefore interfere with the test.

IV. *Determination of the Volume occupied by the Precipitate of Ferric Hydrate produced when the Aqua regia Solution of Pyrites is treated with Standard Alkali.*—In titrating ferric salts with standard alkali and a suitable indicator such as phenolphthalein, it is not possible to obtain satisfactory results when completing the titration with the ferric hydrate precipitate still present. The latter obscures the end-point, and for accurate work the precipitate must be removed. This means making up to a known volume and filtering off an aliquot part for titration. The precipitate occupies a certain volume which should be taken into account and allowed for. To determine this volume a few experiments were made as follows:—

25 cc. pyrites solution were diluted with 200 cc. distilled water, neutralised with $N/1$ caustic soda in slight excess, boiled for a few minutes, and the ferric hydrate filtered off and washed. It was then mixed with a little distilled water, and a specific gravity bottle of known weight was filled with part of the mixture, and the bottle and contents were weighed. The weight of the ferric hydrate in the bottle was then determined by dissolving it in HCl, and titrating with standard titanous chloride and sulphocyanide as indicator. The bottle was refilled with distilled water and again weighed. From these weights it was possible to arrive at (1) the weight (and thus the volume) of the water in the bottle, (2) the weight of water plus ferric hydroxide in the bottle, and (3) the volume of the ferric hydroxide.

Sp. gr. bottle + H ₂ O		= 26.1300
Bottle		= 9.9333
Weight of water		= 16.1967
Bottle + H ₂ O + Fe ₂ (OH) ₆		= 26.2302
Bottle		= 9.9333
H ₂ O + Fe ₂ (OH) ₆		= 16.2969
Weight of H ₂ O + Fe ₂ (OH) ₆		= 16.2969
Fe ₂ (OH) ₆		= 0.1491

Therefore—

$$\text{H}_2\text{O accompanying Fe}_2(\text{OH})_6 \dots = 16.1478$$

The space occupied by the 0.1491 gm. Fe₂(OH)₆ therefore = 16.1967 - 16.1478 = 0.0489 cc. The pyrites contained 41.94 per cent Fe = 80.14 Fe₂(OH)₆. Therefore, if 0.1491 gm. Fe₂(OH)₆ = 0.0489 cc. 0.8014 gm. Fe₂(OH)₆ from 1 gm. pyrites = 0.268 cc.

By similar method 0.1499 gm. of Fe₂(OH)₆ occupied 0.0499 cc., and therefore by proportion the 0.8014 gm. occupies 0.276 cc.

The average of these two last results is that 0.8014 gm. Fe₂(OH)₆ occupies 0.272 cc. Therefore an allowance of 0.27 cc. should be added to the volume to make up for the space occupied by the ferric hydroxide from 1 gm. of pyrites containing 42 per cent Fe. For practical purposes an allowance of from a quarter to one-third cc. will answer quite well.

V.—Having now proved that the nitric acid and hydrochloric acid can be eliminated from the aqua regia solution of pyrites, and that the arsenic is taken up by the precipitated ferric hydrate and thus rendered inactive, and having determined the allowance to be made for the volume occupied by the ferric hydrate, a number of experiments were first made with the aqua regia solution to test the accuracy of the proposed volumetric method of analysis.

The solution of pyrites was prepared as described at the beginning of I. For comparison gravimetric determinations were made simultaneously with the volumetric determinations, and were carried out by the method proposed by Lunge. The author finds that Lunge's method is satisfactory provided that (1) sufficient ammonia is added to ensure that no basic sulphate remains in the ferric hydrate precipitate; (2) the mixture is boiled for a few minutes after addition of ammonia; (3) the ferric hydrate is treated with copious washing of boiling water—the filtrate volume (with 1 grm. pyrites) amounting to about 1600 cc. It is not sufficient (as Lunge says it is) to add ammonia and keep the mixture in a warm place for a time, nor can the ferric hydrate be freed from SO_3 by the comparatively small amount of washing which Lunge recommends, viz., up to 250 cc. for 0.5 grm. pyrites.

The filtrate and washings must be concentrated before adding the BaCl_2 . This evaporation drives out the excess of ammonia, and prevents the formation of too great an amount of ammonium salts which, as Allen and Bishop (*loc. cit.*) show, are deleterious, causing low results.

As already stated, the ferric hydrate carries down any arsenic which may be present, and therefore the BaSO_4 is not contaminated thereby.

The author finds that in Allen and Bishop's method of analysing the pyrites, some of the arsenic present in the pyrites solution finds its way into the BaSO_4 precipitate, but not in sufficient amount to account for the slightly higher results which this method gives. Briefly, their method consists in dissolving the pyrites as previously described, and then reducing the iron to the ferrous condition by means of metallic aluminium powder, excess of which is filtered off. The filtrate and washes are acidified, diluted to 1600 cc., and treated with dilute BaCl_2 solution added drop by drop in the cold. After twelve hours' settling the BaSO_4 is filtered off, ignited, and weighed.

In determining the SO_3 (from the sulphur of pyrites) by titration with standard alkali, phenolphthalein answers very satisfactorily as indicator. The author of this paper finds that it is a reliable indicator for use in determining neutralisable acids. It gives excellent results, provided care is taken to eliminate all carbon dioxide and to keep the liquid briskly boiling during the titration, which is carried out as follows:—

First of all, about 500 cc. of CO_2 free water are prepared. A porcelain basin of about 1000 cc. is used, and into it 500 cc. of water are introduced and slightly acidified with a drop or two of dilute H_2SO_4 . The water is now briskly boiled for two or three minutes to expel CO_2 , a little phenolphthalein solution is added, and then normal soda drop by drop until a permanent pink is obtained.

The pyrites solution (1 grm. in 25 or 50 cc.) is taken in a beaker of about 400 cc. or 500 cc. capacity, diluted to 50 cc. (if necessary), and a measured quantity of standard soda solution is run in (in the cold), and mixed during the addition by stirring or shaking round. About 35 or 36 cc. standard soda are enough, but the exact amount used must be carefully noted after the solution in the burette has thoroughly drained down. The mixture now contains a few cc. of standard alkali in excess, and is brought to the boil, and boiled for about two minutes to ensure decomposition of any basic sulphate lingering in the precipitate. The whole is washed into a 200 cc. flask, cooled to the temperature of the room, made up to 200.3 cc. (0.3 cc. extra to allow for space occupied by the precipitate), well shaken, and filtered through a dry paper and funnel

into a 100 cc. flask, which is rinsed out with the first 25 cc. or thereabouts which come through. 100 cc. of the filtrate are now collected and added to the previously prepared CO_2 free water, made acid with about 4 cc. of normal acid (the exact amount of which is carefully noted), and boiled vigorously for a few minutes to expel all CO_2 . This boiling is continued while standard soda is added drop by drop until the predetermined end-point (the first distinct permanent pink colour) is reached. The amount of alkali used to titrate back is also carefully noted. To calculate the result this last amount of standard alkali is multiplied by two and added to the amount of standard alkali first employed. The total cc. of alkali, if not exactly normal, is calculated to normal, and from this number the cc. of normal acid multiplied by 2 is taken away. The remainder represents the sulphur from 1 grm. pyrites in terms of cc. normal H_2SO_4 , and by multiplying by 0.016 the sulphur in 1 grm. pyrites is arrived at and is easily calculated to per cent.

In cases where hydrochloric acid or nitric acid have not been completely eliminated they must be separately determined and allowed for, as hereinbefore indicated.

Examples.

Ten grms. of finely-ground pyrites were dissolved in aqua regia, the solution evaporated to dryness on the steam-bath overnight, dissolved in distilled water, filtered, and the residue washed. The filtrate and washes were made up to 250 cc. Each 25 cc. = 1 grm. pyrites.

1. 25 cc. of the above solution were treated with moist silver oxide in slight excess in the cold, stirred to coagulate the precipitate, and then filtered, and the precipitate washed free from acid. 35.05 cc. standard alkali were now added to the filtrate and washes, and the whole was brought to the boil and boiled for about two minutes, and then filtered and washed with boiling water till the filtrate came through free from alkali. The filtrate and washes (about 600 cc.) were treated with a few drops phenolphthalein solution, then acidified with 11.5 cc. $n/1$ acid, and boiled for about three minutes to expel CO_2 . Standard alkali was now added until a permanent pink colour was obtained. 5.1 cc. were used.

The total standard alkali = 40.15 cc., which are equal to 40.08 cc. $n/1$ alkali, therefore $40.08 - 11.5 = 28.58$ cc. $n/1$ solution representing the sulphur in 1 grm. pyrites. This multiplied by 0.016 and by 100 = 45.73 per cent S.

By gravimetric analysis the figure obtained by the chemist for the sellers was 45.70 per cent S and for the buyers 45.60 per cent S.

Another 25 cc. of the same solution were neutralised with pure MgO , filtered, and washed, and the HCl determined by titration with $n/10$ AgNO_3 . 0.55 cc. was used. This is equivalent to 0.055 cc. $n/1$ solution, and is to be deducted from the amount arrived at in the next test.

2. 25 cc. of the same solution were diluted and treated with a smaller excess of standard alkali than was used in I. 32.65 cc. in all were used, and this is equivalent to 32.59 cc. $n/1$; exactly 4 cc. of $n/1$ acid were taken. Therefore $32.59 - 4 = 28.59$ cc. $n/1$ solution.

$$28.59 - 0.055 \text{ (allowance for HCl)} = 28.535.$$

$$28.535 \times 0.016 = 0.4566 = 45.66 \text{ per cent S.}$$

A fresh solution of the same pyrites was made up as follows:—10 grms. were dissolved in aqua regia, the solution evaporated to dryness, about 20 cc. of water were added, and the solution again dried up, and left on the steam over the week-end. The residue was dissolved in distilled water, filtered, &c., and made up to 250 cc. 25 cc. (1 grm. pyrites) tested for HCl contained equal to only 0.02 cc. $n/1$.

25 cc. of the above solution were now added to 300 cc. tap (Manchester) water, and treated with 32.02 cc. standard alkali, boiled for a few minutes, cooled, made up to 500.3 cc., and 250 cc. were filtered off. This portion (half of the total) was acidified with 3.05 cc. $n/1$ H_2SO_4 , boiled, and titrated back with standard alkali equal to 1.35 cc.

Therefore, $32.02 + (1.35 \times 2) = \text{total alkali} = 32.02 + 2.7 = 34.72$ cc. standard alkali.

This 34.72 cc. = 34.66 cc. *n/l*. $34.66 - (3.05 \times 2) = 28.56$ *n/l* solution representing the total acidity.

$28.56 - 0.02$ (for the HCl present) = 28.54 and $28.54 \times 0.016 = 0.4567$, which equals 45.67 per cent S.

VI. *Determination of the Sulphur after Oxidising the Pyrites by means of Dilute Nitric Acid and Bromine.*—10 grms. of finely-ground pyrites (from the Pena Copper Mines in Spain) were treated with 100 cc. $\text{H}_2\text{O} + 100$ cc. HNO_3 . When the action was over some S remained unoxidised, so cooled to 50°C . and added 5 cc. bromine and warmed upon the steam, and then boiled till brown fumes ceased to come off. On evaporating to dryness, moistening with water, and heating, a faint smell of HNO_3 was perceptible. On determining the nitric acid it was found to be equivalent to 0.5 cc. *n/10* $\text{KMnO}_4 = 0.00027$ gm. S per 1 gm. of pyrites; therefore, 0.03 is to be deducted from the final per cent of S found.

The 10 grms. pyrites, after solution, were made up to 250 cc., so that each 25 cc. equals 1 gm. pyrites.

25 cc. + 25 cc. $\text{H}_2\text{O} + 35.07$ cc. *n/l* NaOH were boiled for a few minutes, cooled, and made up to 200.25 cc. 100 cc. filtered off, added to 400 cc. CO_2 -free boiling water, then acidified with 4 cc. *n/l* acid, boiled a few minutes, and titrated at the boil with *n/l* alkali and phenolphthalein as indicator took 1.66 cc. *n/l* alkali.

$35.07 + (1.6 \times 2) - (4 \times 2) = 30.27$ cc. *n/l*.

$30.27 \times 0.016 = 48.43$, and this figure less 0.03 allowance for the HNO_3 left in the solution = 48.40 per cent S.

Another test on the same lines came to 48.35.

By gravimetric analysis, the sellers of this pyrites made the sulphur 48.30 per cent and the buyers made it 48.40 per cent.

Another sample of Foldal pyrites from Norway was tested in the same way. After solution in dilute nitric acid and bromine, and evaporating to dryness and then dissolving in water, and filtering and washing up to 250 cc., the amount of nitric acid left in each 25 cc. was found to be equivalent to 0.04 on the per cent of sulphur.

25 cc. + 25 cc. $\text{H}_2\text{O} + 35.00$ cc. *n/l* soda were boiled a few minutes, cooled, and made up to 200.25 cc. 100 cc. filtered off and titrated as before used 4 cc. *n/l* acid and 0.9 cc. *n/l* alkali; $35.00 + (0.9 \times 2) - (4 \times 2) = 28.8$ cc. *n/l*. $28.8 \times 0.016 = 46.08$ —deducting 0.04 gives 46.04 per cent sulphur.

Another test, but making up to 500.25 cc. after adding the 35 cc. *n/l* alkali, gave a percentage of 45.94 of S.

By gravimetric analysis the buyers made this 45.9 per cent, the sellers made it 46.47 per cent, and the referee (Claudet) made it 45.7 per cent.

Another sample of pyrites from Spain, after treatment with dilute nitric acid and bromine, evaporating to dryness, moistening with water, and heating in the air-bath for two hours at 110°C ., was found to have in the solution nitric acid equal to only 0.01 S on the per cent of sulphur. Two titrations were made, and gave 49.26 per cent S and 49.14 per cent S. Sellers' figure = 48.2, buyers' = 49.2, and the referee (Claudet) made it 49.0, all being by gravimetric analysis.

Another sample of pyrites from Spain, after oxidation with dilute nitric acid and bromine, drying on the steam overnight, and then in the air-bath at 110°C . for an hour, gave a solution quite free from HNO_3 .

By titration the sulphur came to 46.98 per cent. The buyers, by gravimetric analysis, made it 46.2; the sellers, 47.1; and the referee, 47.0 per cent.

Two solutions were made of another pyrites from Spain (1) by dilute nitric acid and bromine, &c.; (2) by aqua regia ($1\text{HCl} + 3\text{HNO}_3$), evaporating to dryness, moistening with HCl, and leaving to dry on the steam overnight.

Both solutions were found free from HNO_3 , and (2) contained HCl equal to only 0.2 cc. *n/10* AgNO_3 per 1 gm. pyrites.

This amounts to 0.02 cc. to be deducted from the total

n/l alkali used per gm. pyrites. (1) Gave 48.43 and 48.5 per cent sulphur; (2) gave 48.56 per cent. The buyers, by gravimetric analysis, made the S 48.4 per cent. and the sellers made it 48.3.

VII. A series of tests were made, using varying amounts of standard alkali. The pyrites employed was a sample of washed Pena (that is, a pyrites which has been treated by a system of washing with water to recover the copper). The solution in dilute nitric acid and bromine, after drying on the steam overnight, moistening with water, and heating for one hour at 110°C . in the air-bath, was found free from HNO_3 . Gravimetrically, the sulphur was found to be 46.1 per cent by another chemist. 0.1 gm. of pyrites this is equivalent to 28.81 cc. *n/l* alkali.

Six trials were made, and the results are shown in tabular form, thus:—

	Cc. standard alkali added at first.	Net cc. = S.	Per cent S.
Theory ..	—	28.81	46.10
No. 1. ..	31.05	28.78	46.04
" 2. ..	32.10	28.78	46.04
" 3. ..	33.12	28.76	46.02
" 4. ..	35.05	28.86	46.18
" 5. ..	38.05	28.84	46.14
" 6. ..	35.00	28.75	46.00

Nos. 1 to 5 were boiled for five minutes after the addition of the alkali, whereas No. 6 only had one minute, which would appear to have been hardly enough.

At this stage an experiment was made to ascertain the effect of using a standard alkali containing an appreciable amount of carbonic acid. A normal solution was made up containing 5 parts Na_2CO_3 to every 95 parts NaOH, and it clearly came out that CO_2 in the alkali tends to give high results when a comparatively large excess is used. The results obtained are tabulated thus:—

	Cc. alkali added.	Net cc. = S.	Per cent S.
By gravimetric analysis ..	—	(30.78)	49.25
Experiment 1. ..	32	30.74	49.18
" 2. ..	35	30.94	49.50
" 3. ..	40.15	31.25	49.90

Conclusion.—The standard alkali should be as free as possible from carbonic acid.

VIII. The results recorded in the preceding pages, together with a few more analyses of other pyrites samples, are collected and tabulated below to illustrate the efficiency of the new volumetric method as compared with gravimetric analysis.

Description of pyrites.	Gravimetric analysis.	Volumetric analysis.	Diff.
Foldal (Norwegian) ..	45.65	45.73	+0.08
Pena (Spanish) ..	48.37	48.35	-0.02
Foldal (Norwegian) ..	45.99	45.80	-0.19
Pena (Spanish) ..	49.10	49.20	+0.10
Pena (Spanish) ..	48.35	48.47	+0.12
Washed Pena (Spanish) ..	46.10	46.18	+0.08
Cupreous pyrites ..	44.00	44.11	+0.11
Low grade pyrites ..	36.25	35.12	-1.13

This last ore contains 2.3 per cent CaO , equivalent to 1.31 sulphur.

Concluding Remarks.—It goes without saying that special care must be taken to have the strength of the standard acid and alkali accurately determined. First the sulphuric acid, and from it the alkali; the standardisation being carried out under the same conditions as in the test.

The advantage of this volumetric process of analysis is, of course, a great saving of time and trouble, combined at the same time with accuracy.

SOME MAIN LINES OF ADVANCE IN THE DOMAIN OF MODERN ANALYTICAL CHEMISTRY.*

By A. CHASTON CHAPMAN.

(Continued from p. 257).

I WILL now turn for a brief space to another side of my subject. If organic chemistry by its rapid growth, vast importance, and all-compelling interest was responsible for the temporary neglect of analytical chemistry at one stage of its history, it has since made ample amends by furnishing the analytical armory with a number of very important weapons. If it has presented to the analyst innumerable problems of the highest importance, it has also supplied in many cases the means for their solution. To speak more plainly, it has been found during recent years that many of the more or less complex products of the organic laboratory are, in fact, very valuable analytical reagents, and that by their use old problems may often be better solved and new ones successfully attacked.

One of the earliest of these was phenylhydrazine, by the discovery of which in 1878 E. Fischer placed in the hands of chemists a reagent which is now almost as necessary in the analytical as in the purely organic laboratory. In qualitative analysis, it is only necessary to refer to the application of the osazone reaction to the identification of the various sugars, a problem the difficulty of which is only equalled by its importance, whilst in quantitative analysis it has a large sphere of usefulness in the estimation of aldehydes and in the quantitative examination of compounds containing the carbonyl, nitroso-, and nitro-groups. In addition to phenylhydrazine itself, considerable use has been found for some of its substituted derivatives, such as *s*-phenylmethylhydrazine, *s*-diphenylhydrazine, and the *p*-bromo- and *p*-nitro-compounds. In this connection, reference may also be made to *β*-naphthylhydrazine, a substance which Ekenstein and Lobry de Bruyn have shown to be of great service in the recognition and separation of certain carbohydrates and for the estimation of vanillin, and to semicarbazide, a substance which has proved so useful in the isolation and identification of the aldehydic and ketonic constituents of many essential oils.

As further examples of organic compounds which have been successfully applied to the identification and estimation of organic substances of technical importance, mention may be made of phloroglucinol, digitonin, picric acid, and picrolonic acid. The estimation of pentoses and pentosans in certain foodstuffs and in many agricultural products is often a matter of importance, and, as is well known, the method almost invariably adopted consists in distilling the substance under investigation with hydrochloric acid and estimating the furfural in the distillate. For this purpose, phloroglucinol, which forms with furfural a sparingly soluble compound—the so-called phloroglucide—is often made use of. In the same way, methyl-pentoses and methyl-pentosans can be estimated as the corresponding phloroglucinol compound. Further than this, the difference in the solubility in alcohol of the two phloroglucides affords a means for the approximate separation of the pentoses (for example, arabinose and xylose) and the methylpentoses (for example, rhamnose and fucose).

In 1910 Windaus made the discovery that one molecule of cholesterol is capable of uniting with one molecule of digitonin to form a compound of high molecular weight ($C_{82}H_{140}O_{29}$) which is very insoluble, and can consequently be conveniently employed for the estimation of the former substance—a matter of considerable importance to physiological and occasionally to technical chemists. Since digitonin also forms a similarly insoluble compound with phytosterol, it has been employed for the purpose of obtaining either or both of these alcohols in a pure con-

dition prior to converting them into their acetates, as in the ordinary Bömer test. In this way, the detection of vegetable oils of animal origin, or vice versa, is much facilitated.

The extensive use made of picric acid for the identification, and occasionally for the estimation, of alkaloids and other bases is too well known to need more than a passing reference, and more recently picrolonic acid (dinitrophenylmethylpyrazolone) has been employed for the same purpose. The picrolonates are in some cases less readily soluble than the corresponding picrates, crystallise well, and are often very characteristic. The importance of adding to our means of identifying such substances as arginine, histidine, lysine, guanidine, and other physiologically important bases will be obvious to all who have followed the developments of modern biochemistry.

It will be seen that the instances I have given above are all cases in which one organic compound has been made use of for the identification or estimation of another. I will now refer to a more interesting and, in a sense, more significant application of certain organic compounds, namely, to the detection and estimation of what may be conveniently described as the simpler inorganic acids and bases.

One of the earliest of these is the *m*-phenylenediamine test for nitrous acid, for which we are indebted to Peter Griess. Already in 1870 Griess had recommended the use of one of the diaminobenzoic acids for the detection of nitrous acid, and in 1878 he proposed the use of the above reagent as being much more sensitive, and the method was worked out on the quantitative side about the same time by Preusse and Tiemann. In the following year Griess published a further paper, in which he recommended for the same purpose the use of a mixture of sulphanilic acid and *α*-naphthylamine—a method which is occasionally ascribed to Ilosvay, who merely recommended the substitution of acetic acid for a mineral acid as the acidifying medium.

Another well-known colorimetric method for the detection and estimation of minute quantities of nitrous and nitric acids is due to Lunge, and involves the employment of diphenylamine. Although, unfortunately, not specific, it has proved of the greatest service in the estimation of minute traces of nitrogen acids in sulphuric acid, milk, and other technical products.

A good many other organic compounds, such as phenol-sulphonic acid and resorcinol, have been recommended at various times for the detection and estimation of nitrates and nitrites, but it will not be necessary to refer to these in any detail. It will, of course, be readily understood, that the nature of my subject—even if time permitted—renders it unnecessary for me to deal by way of illustration with more than a few of the instances in which organic compounds have been pressed into the service of this branch of general analytical chemistry, and I shall confine my attention to those methods which have been very thoroughly tested and have been elevated to the rank of standard processes.

Whilst dealing with the estimation of commonly occurring inorganic acids, mention may be made of the benzidine method for sulphuric acid and the use of "nitron" for the estimation of nitric acid. The former method, which owes its origin to W. Müller, depends on the fact that benzidine sulphate is almost entirely insoluble in cold water in the presence of an excess of benzidine hydrochloride, and since the method is a volumetric one, it possesses the advantage of rapidity.

Notwithstanding that it has been studied and recommended for special purposes by such experienced workers as Raschig and G. v. Knorre, it is obviously very unlikely that any organic compound will ever replace barium as a general reagent for the estimation of sulphuric acid. I have referred to this method rather in the hope that it may stimulate investigation in this direction, since the occurrence of an insoluble sulphate of an organic base, and still more the discovery of an insoluble nitrate, such as is

* A Lecture delivered before the Chemical Society, March 15, 1917.

referred to below, render it probable that similar insoluble salts, suitable for analytical purposes and possibly representing some well-defined advantages over existing methods, still remain to be discovered.

In 1905, in the course of an investigation of the *endo*-iminotriazoles, Busch observed that these bases are characterised by the formation of very sparingly soluble nitrates. By a fortunate chance, it happened that the most readily prepared of these compounds, namely, 1 : 4-diphenyl-3 : 5-*endo*-anilo-4 : 5-dihydro 1 : 2 : 4-triazole, was the one which gave a nitrate possessing the highest degree of insolubility. One molecule of this base unites with one molecule of nitric acid, giving a compound of the formula $C_{20}H_{16}N_4$, HNO_3 , and it is capable of giving a precipitate in a solution containing as little as 1 part of nitric acid in 80,000 parts of water.

This base, which can be obtained commercially under the more easily remembered and more euphonious name "nitron," is very easily employed as a reagent, and furnishes us for the first time with a means of making a direct gravimetric estimation of nitric acid. It has been applied with success to the estimation of nitrates in water and in a considerable number of commercial products, such as natural nitrates, nitrocellulose, soils and plants, and is particularly well suited for the estimation of nitrates in liquids containing much organic matter. It has also been found that the method is applicable to the estimation of picric acid, since 1 part in 250,000 parts of water gives a precipitate of the "nitron" picrate. The discovery of unexpectedly useful properties, such as the insolubility of this nitrate—and many other striking examples might easily be quoted—adds a great attraction to the study of pure, synthetic organic chemistry.

I will now pass for a few moments to the application of organic compounds to the quantitative separation and estimation of many of the commoner and some of the rarer metals.

One of the first substances to be used for this purpose, and one which is susceptible of somewhat wide application, is nitroso- β naphthol, which has been very thoroughly studied by G. v. Knorre and his colleagues. It has been found, for example, that by the use of this reagent nickel may be separated from cobalt; iron from aluminium; copper from cadmium, magnesium, manganese, zinc, mercury, and lead; iron from manganese, zinc, nickel, and chromium; iron from glucinum; copper, iron, and cobalt from antimony and arsenic; and iron from zirconium.

Many of these separations can be effected with ease and with accuracy, the metallic derivatives of the nitroso- β -naphthol being easily dealt with, and being, of course, readily converted by ignition into the corresponding oxides. The copper compound has the formula $(NO.C_{10}H_6O)_2Cu$.

m-Nitrobenzoic acid has been successfully used for the quantitative separation of thorium from cerium, lanthanum, and didymium in the analysis, for example, of monazite sands, whilst palladium can be readily separated from platinum and other metals of the platinum group by means of acetylene.

De minimis non curat may be true of the law, but it certainly is not true of modern chemistry, which in certain directions is almost coming to be regarded as the chemistry of traces. The importance to the physiological chemist, to the metallurgical chemist, and to the food chemist of being able to detect with certainty small traces of substances is well recognised, and peculiar interest therefore attached to Tschugaev's observation in 1905 that dimethylglyoxime constitutes a delicate test for nickel. He showed, in fact, that it was capable of detecting 1 part of the metal in more than 1,000,000 parts of water, and of affording certain indications, even when cobalt was present to the extent of 5000 times that of the nickel. The reaction may be represented by the following equation:— $2C_4H_8O_2N_2 + NiCl_2 + 2NH_3 = (C_4H_7O_2N_2)_2Ni + 2NH_4Cl$.

This method has been very thoroughly investigated by many chemists, some of whom have introduced modifica-

tions with the object of increasing its sensitiveness. Thus, it has been quite recently stated that, by the adoption of certain modifications, as little as 0.02 mgrm. can be readily detected in 50 c.c. of solution, whilst some years ago Armit and Harden state that they were able, when working with pure nickel sulphate, to detect as little as 0.001 mgrm. in 30 c.c., whilst 0.003 mgrm. gave a very marked pink colour in that volume of liquid.

As a reagent for the colorimetric estimation of traces of nickel, dimethylglyoxime possesses very great and obvious advantages over the ammonium sulphide method. The coloration is more characteristic, traces of iron do not interfere, and the method is, of course, much more sensitive.

As a means of estimating nickel in alloys, particularly in the presence of cobalt, zinc, and iron, this method has proved exceedingly useful, being rapid and possessed of a tolerably high degree of accuracy.

Another oxime, namely, α -benzildioxime, originally described by Tschugaev, has been recommended by Atack for the qualitative detection of nickel and for its estimation. It forms an intensely red nickel compound having the formula $C_{28}H_{22}O_4N_4Ni$, containing only 10.9 per cent of nickel. It is even more sensitive than dimethylglyoxime, and it has been stated that with this reagent, 1 part of nickel in 10 million parts of water can be detected. Like dimethylglyoxime, it has been recently utilised for the detection of traces of nickel in hardened edible fats, in which nickel has been used as a catalyst. When working on 50 grms. of the fat, 1 part of nickel in 5 million parts of the fat can be detected. It is of interest to note, in passing, that the β isomeride does not yield the nickel reaction.

Another organic compound utilised during recent years for the estimation of nickel is dicyanodiamidine. This reagent, which was originally recommended by Grossmann in 1906, is used in the form of the sulphate, and the nickel compound, which is a well-crystalline, yellow substance, has the composition $N_4(C_2H_3ON_3)_2 \cdot 2H_2O$. By the use of this reagent, nickel may be separated from cobalt, iron, chromium, zinc, and other metals, and, given suitable conditions, may be estimated with a high degree of accuracy. It has, in fact, been used very largely, particularly in Continental laboratories, for the analysis of German silver, commercial nickel, nickel steel, and other alloys. Although it is not by any means as sensitive as either of the two above-mentioned reagents, it is said to be capable of detecting 0.5 mgrm. of nickel in the presence of as much as 1 grm. of cobalt.

The above methods for the estimation of nickel are of great technical importance, since the precipitates are crystalline and form readily at the ordinary temperature. They can be filtered with ease, they are of constant composition, and the percentages of nickel are not high. The employment of these more or less complicated organic reagents is, as I have indicated, of comparatively recent introduction, and it is not too much to hope that similarly serviceable methods will be discovered for the separation and for the rapid and accurate estimation of other closely allied elements.

In 1909 Baudisch discovered that the ammonium salt of nitrosophenylhydroxylamine $(C_6H_5N[NO]ONH_4)$ was capable of being used for the quantitative precipitation of iron and of copper, and for the separation of these metals from a number of others with which they are frequently associated in practice. This substance, to which the simpler name "cupferron" has been applied, has been found to be capable of somewhat wide application, and has proved a valuable addition to our laboratory reagents.

Ferric iron is precipitated completely in cold solutions containing hydrochloric, sulphuric, or acetic acids as the compound $(C_6H_5N[NO].O)_3Fe$, and may readily be separated from aluminium, chromium, and indeed from most other of the common metals, including, by a special process, even copper.

The method has proved useful for the separation and

estimation of iron in a number of commercial products, and R. Fresenius, who has submitted it to a critical study, states that the separation of iron and aluminium can be carried out more conveniently and with greater accuracy by the use of this substance than by any other gravimetric method.

I do not propose to enter into any details of the various separations effected by this reagent, but will confine myself to pointing out that by its aid copper may easily be separated from cadmium, zinc, and many other metals, and that both titanium and zirconium may be separated from iron and from aluminium. The titanium compound is a bright yellow substance having the formula $(C_6H_5)_3N[NO](O)_4Ti$.

As an example of the degree of accuracy which may be reached in these separations, it may be pointed out that, when quantities of iron varying from 0.03 grm. to 0.3 grm. were precipitated in the presence of quantities of aluminium and chromium equal to fifty times the weight of iron present, the error rarely exceeded ± 0.2 mgrm. I mention this detail merely for the purpose of showing that in the case of these complex organic reagents, the many advantages which are frequently obtained are not necessarily secured at the expense of accuracy.

I think I have dealt at sufficient length with this division of my subject, and I will now turn for a few moments to the consideration of a third main line of advance, namely, that concerned with the utilisation of what may be conveniently called biological methods. In the future we may succeed in synthesising enzymes and even precipitins, but that day is not yet, and for some time to come we must remain dependent on the activity of the living organism for the reagents to which I am now referring.

With the mechanism of enzyme action we are not now concerned. What is of importance from the analytical point of view is its specific character. To such an extent is this the case that the enzymes are actually capable of discriminating between certain of the carbohydrates and their optical isomerides. Thus, *d*-glucose, *d*-mannose, *d*-fructose, and *d*-galactose are fermentable by yeast, whilst their optical isomerides are unfermentable.

In order that a given sugar other than the four above mentioned may be fermented, it is essential that the yeast employed should contain the enzyme necessary for its conversion into one or other of those hexoses. Now yeasts of different species do not all contain the same enzymes, and it happens, therefore, that a certain species of yeast may be capable of fermenting one carbohydrate and incapable of fermenting another.

Of the various enzymes, invertase is one of the most widely distributed among the saccharomycetes, and consequently the great majority of yeasts are capable of fermenting sucrose. On the other hand, lactase occurs in only a comparatively small number of species, and consequently a great many yeasts, including the ordinary brewers' yeast, are incapable of fermenting lactose.

The following table may be of interest as showing at a glance the behaviour of certain of the yeast species towards several of the more commonly occurring sugars:—

	Dex- trose.	Fruc- tose.	Man- nose.	Galac- tose.	Malt- ose.	Suc- rose.	Lac- tose.
<i>Sacch. cerevisiae</i> ..	+	+	+	+	+	+	o
<i>Sacch. cerevisiae</i> , Carlsberg ..	+	+	+	+	+	+	o
<i>Sacch. Pastorianus</i>	+	+	+	+	+	+	o
<i>Sacch. ellipsoideus</i> .	+	+	+	+	+	+	o
<i>Sacch. Marzianus</i> ..	+	+	+	+	o	+	o
<i>Sacch. exiguus</i> ..	+	+	o	+	o	+	o
<i>Sacch. Ludwigii</i> ..	+	+	+	o	o	+	o
<i>Sacch. anomalus</i> ..	+	+	+	o	o	+	o
<i>Sacch. fragilis</i> ..	+	+	+	+	o	+	+
Kefir ..	+	+	+	o	o	+	+

The sign + indicates that the yeast in question is

capable, and the sign o that it is incapable, of bringing about fermentation.

The secretion of any particular enzyme appears to be a very constant attribute of a given species, and it has not been found possible by varying the nature of the food supply or the general environment of a given species to cause it to secrete other enzymes than those normally present. It is this constancy of enzyme production and this selective character that render certain of the yeast species so useful to the analyst, enabling him to arrive at the composition of complex carbohydrate mixtures, the analysis of which would be impossible by any other means.

The method is clearly one which must be applied with caution, and it demands, moreover, some biological training on the part of the operator. The technique, however, is not difficult, and at the present day the majority of analytical chemists, particularly those who are concerned with the analysis of foodstuffs, realise that a certain amount of training in elementary bacteriology is a necessary part of their professional equipment.

It will, of course, be clear that, in addition to yeasts, other organisms which secrete enzymes, such as moulds, may be utilised for analytical purposes, and the preparation of Taka-diastase from *Aspergillus oryzae* is an illustration in point. *Torulæ*, again, have recently been pressed into the service, since some of these, unlike the yeasts, do not contain any invertase, and so are capable of fermenting away dextrose and fructose, leaving sucrose unattacked. Biological methods such as I am now referring to are in everyday use in the analysis of many sugar products, such as commercial glucoses and invert-sugars, and find extensive employment in the analytical examination of complex carbohydrate mixtures such as many of the prepared foods intended for infants and for invalids.

As one further example of the usefulness of this method, it may be pointed out that, whilst the top yeast as obtained in English breweries converts raffinose into fructose and melibiose, the bottom yeast as obtained in Continental breweries, which contains melibiase as well as invertase, converts it into fructose, galactose, and dextrose, that is to say, into completely fermentable products. It is therefore possible by employing these two types of yeast, and by making a simple polarimetric observation, to estimate the amount of raffinose present in a mixture of sugars—a problem which only a few years ago would have been considered impossible of solution.

Another "analytical" method of a more definitely biological character, but one which has already shown itself to be of great practical importance, is that depending on the "precipitin" reaction—a reaction which permits of the identification of so-called homologous proteins and their differentiation from others which they resemble so closely that they are indistinguishable by purely chemical means. The principle underlying the method is that if a solution of any given protein be injected into the blood of an animal, the blood serum of that animal will produce a precipitate with an infusion containing the particular protein injected, but not with any other. Thus, if horse-blood serum be injected into a rabbit, the serum of the rabbit's blood will produce a precipitate when added to an extract of horseflesh, but not with an extract of any other kind of flesh. It thus becomes possible by means of this method to identify horseflesh in mixed foodstuffs, such as sausages. It is also possible to detect small quantities of castor seeds in feeding cakes, to distinguish between hen-egg albumin and the albumin of the eggs of other birds, between the milk of one animal and that of another, between genuine and artificial honey, and even, so it is stated, between the seeds of two-rowed and of six-rowed barley. The importance of the reaction for the identification of human blood in medico-legal investigations is well recognised.

(To be continued).

NEW FLAVIN ANTISEPTIC.

ITS DISCOVERER, DR. BROWNING, BEFORE THE PATENTS COURT. HOW PAUL EHRLICH HIT ON THE NAME.

A CORRESPONDENT sends the following communication:—

The discovery of the new antiseptic, Flavin, which comes originally from coal-tar, was discussed in the Patents Court on Thursday, May 24, when Dr. Browning was present and made a statement, and an interesting document was forthcoming on the investigations of Paul Ehrlich. The court at the same time debated the name by which the antiseptic is henceforward to be known. A report of earlier proceedings appeared in a recent issue of the CHEMICAL NEWS.

Mr. McKenna now suggested a name, on behalf of the Boots Pure Drug Company, who, with Messrs. Levenstein, Ltd., Manchester (represented by Mr. Colefax, K.C.), Messrs. May and Baker, and Messrs. T. Kerfoot and Co., Manchester (represented by Mr. Armstrong, of Messrs. W. P. Thompson and Co., Liverpool), asked for licence to manufacture the substance, under the German patent 24652 of 1910, and raised the question of the suspension of the trademark 327437, which applies to it the name "Trypa-Flavin." The patent is in the name of Messrs. Cassella (for whom Mr. Ransford appeared), and Messrs. Cassella, it was complained, unless something was done, would re-enter the market after the war and supply the specific under the trademark name. The problem was to find a generic name which would cover the several manufactures of all these firms, and not lead to the misconception, after the war, that the original and proprietary article was alone to be obtained of Cassella. The patent, of course, is for a yellow dye, whereas the honour of the discovery of the pre-eminent value of Flavin as a war antiseptic belongs to Dr. Browning and his coadjutors of the Bland-Sutton Institute. Dr. Browning's name heads the report made by the Institute to the Medical Research Committee on its rapid curative properties, as demonstrated at the Middlesex Hospital.

Dr. Browning told the Court how he came to use the name in its more popular and abbreviated form. When he took his seat in the witness-chair, the Controller of Patents (Mr. Temple Franks) said: "We all agree, Dr. Browning, that it is largely due to you that the discovery was made that the substance has this peculiar property."

Dr. Browning replied that he supposed that before the work he and those associated with him undertook, there was no knowledge that this substance was an antiseptic.

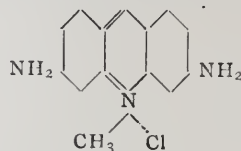
The Controller: The knowledge is due to purely independent British research work.

Dr. Browning said that Ehrlich experimented with 3.6-diaminoacridinium, and gave the compound he obtained the name Trypa-Flavin. "I was loth," added Dr. Browning, "because of the respect I have for Ehrlich's memory, to interfere with any word used by him. When we agreed to speak of the substance simply as Flavin, there was no commercial consideration. It was a convenient abbreviation to close out the first syllable, and 'Trypa' was certainly not suitable for general use. It belonged to the period of certain experiments in respect of sleeping sickness. 'Flavin' could be used with various prefixes."

Mr. Francis H. Carr, of Boots Pure Drug Company, said they favoured, for their own use, the term "Acri-Flavin." "Septo-Flavin had also been suggested. Mr. Carr put in a translation he had made upon the origin by Ehrlich of the trademark name, of a passage in a German book, "Paul Ehrlich, a Presentation of his Scientific Life" (Jena, 1914). The translation runs:—

"Since, however, the quotient, curative dose : toxic dose (in the case of acridinium yellow) proved to be too high, that is to say, unfavourable, and since Ehrlich had observed elsewhere—e.g., in comparing Fuchsin with Parafuchsin—that methyl-groups attached to the nucleus have a dystherapeutic action, he induced L. Benda to

prepare the lower homologue of acridinium yellow, namely the 3.6-diamino-10-methyl-acridinium chloride (formula III.)



"For this purpose it was necessary, in the first place, to seek a practicable method for preparing 3.6-diaminoacridine, which had hitherto been obtainable with difficulty. The search for such a method was successful, and the transformation into the acridinium derivative presented no further difficulties. The new preparation shows now, indeed, the superiority expected by Ehrlich over the homologous acridinium-yellow; with doses of similar toxicity its trypanocidal power is about three times as high as that of the homologous compound, so that the latter is a further example of the dystherapeutic action of the CH₃ group. The compound received from Ehrlich the name of Trypa-Flavin. Mice of 20 grms. body-weight, which had been heavily infected with a specially virulent strain of trypanosomes, could be regularly cured by a simple injection of a cubic centimetre of 1 gm. of trypa flavin in 5500 grms. of water."

The Controller of Patents, who sat with Sir Cornelius Dalton, observed that they had been in consultation with the Medical Research Committee and the National Health Committee, and had come to the conclusion that they must not allow the manufacture of any applicant firm to be put on the market except under substantially the same name. They wanted the most suitable and the most convenient.

Mr. Colefax, for Messrs. Levenstein, said that "Septo-Flavine" was their suggestion. They had supplied to the War Office under the title "Wound Antiseptic, Avalin Brand," and they were likely to continue to use the brand name for whatever they manufactured.

Mr. McKenna asked that, as there was as yet no commercial demand and as they had the goodwill to build up—and as, moreover, the substance was expensive to manufacture—the Board of Trade should be content with a nominal royalty, say 1 per cent.

Mr. Colefax remarked that he had come prepared to offer 2½ per cent!

The Controller answered that he did not gather that Flavin could ever be a cheap substance. It was used in the proportion of one to 1060 in water, so that a ton represented an enormous quantity. He did not understand that it was likely to be sold to small retailers. In fixing royalty acknowledgment, they had to remember that the patent was a dye, and the British use was for something else. The matter, too, was in its experimental stage. There might be by-products or intermediate products waiting to be discovered, which would lead to yet other results. The matter was still under research and investigation.

Mr. W. Colebrook Reynolds, F.I.C., B.Sc., of Jeyes Sanitary Compound Company, said he had gone to some pains to find out the practice, and he saw that "Trypa-Flavin" was used as the recognised name in all the textbooks, German and English. He suggested that the trademark registered should be voided, and that this term should be taken for general use. There would then be no proprietary right in it left. The employment of the prefix "methyl" would only apply to one form of the substance. There were other derivatives to think of. The acridinium bodies could be modified in various ways. "Trypa-Flavin" was specially applicable to the use of the body in sleeping sickness.

The Controller of Patents, in the end, announced that the court would have no hesitation in recommending that licences be granted to all the applicant firms to manu-

facture. The court would consider whether the trademark should be continued. A condition of the licence would have to be that no other substances of similar kind, intermediate or derivative, should be sold by the licencees except under names to be approved by the Board of Trade. The Board wished to secure that the same product was not put on the market by different manufacturers under different names. But with the name to be approved, manufacturers would not be precluded from using their own brand name or trademark. Honestly, he did not think the royalty mattered much. The terms could always be revised, and he saw strong grounds for putting the royalty at a low rate. The real merit of the discovery, it had to be insisted, lay with Dr. Browning and his coadjutors. It was not in the least a case where the peculiar value had been made by the patentee. That had always to be borne in mind. The Board would examine the advantages of the scientific name—he thought “acri-flavine” was a fairly good title—and they would consider also whether the royalty should be 1 or 2½ per cent. The applicants would hear as to their licences in due course.

HEALTH AND INSECT LIFE IN WAR AND PEACE.*

By A. E. SHIPLEY, Sc.D., F.R.S.,
Master of Christ's College, Cambridge; Lecturer on Zoology,
University of Cambridge.

THE lecturer dealt with a number of insects which are a nuisance in times of peace and a veritable pest in times of war. Owing to the aggregation of large numbers of men, with infrequent opportunities of washing themselves, these insects breed and multiply exceedingly.

The insects which affect armies fall roughly into two categories: those which pierce the skin of man and convey disease, or the animals upon which the soldiers are dependent, e.g., the horse, and those which interfere with and diminish his food supplies. Again, the latter class may be subdivided into those which diminish the amount of available food and those which infect food with pathogenic germs such as those of enteric fever.

The lecturer proceeded to describe one of the curses of an army—the body louse—which, although so prolific in the field, is difficult to rear in the laboratory. He then passed on to the bed bug, which, he remarked, only appeared in England about 400 years ago, early in the reign of King Henry VIII. Apparently, like the black and the brown rat, it came from the East and was for a time confined to our seaports and harbours. He described the life-history of the insect, and its singularly successful method of getting on to its prey. The louse is responsible for the spread of typhus. The bed bug has been accused of conveying many diseases. Certainly in the laboratory it does act a vector of these diseases, but whether it does so on a large scale in ordinary life is not so certain.

But the flea is undoubtedly a conveyor of plague from rats to rats and from rats to man, and its life history and characteristics deserve the utmost attention.

Leaving the crawling and walking insects, and coming to those that fly, Dr. Shipley then passed on to insects such as the mosquito, which has probably played a bigger part in the history of the world than any other organism except man. Certain species of it convey malaria, which was the cause, according to some classical authorities, of the decadence of Greece and the decay of the Roman Empire. It first passed into Rome at the time of the second Punic war, the war which Dr. Johnson hoped “would never again be mentioned in his presence.” It took some 200 years to get from Rome as far north as Ravenna. Another mosquito, *Stegomyia*, is a carrier of yellow fever, and a third insect, the sand-fly, has caused infinite trouble to the troops in Salonika, Egypt, and Mesopotamia.

After a brief reference to the insects which play so large a part in destroying the hides or potential leather of the country, the lecturer passed on to the habits of the house-fly, whose conveyance of infantile diarrhoea is so pronounced. In conclusion he drew attention to certain insects which destroy the “hard tack” of our Navy and interfere with the flour mills of the country. One species of this insect infests at least 50 per cent of the figs in the East—a matter of some consideration when we reflect upon the number of our soldiers who are fighting in the fig-producing countries.

CAPITAL AND LABOUR IN CO-OPERATION.

NATIONAL ALLIANCE OF EMPLOYERS AND EMPLOYED.

A MEETING of the General Committee of the National Alliance of Employers and Employed was held on May 22 at the headquarters of the Alliance, 64, Victoria Street, London, S.W., when, after a full discussion, the new constitution was adopted. The Hon. Frederick Huth Jackson (Chairman) presided, and among those in attendance were Mr. W. A. Appleton (General Federation of Trade Unions), Mr. J. M. Bell (National Union of Labour), Mr. H. H. D. Anderson (Associated Portland Cement Manufacturers), Sir K. Crossley, Bart. (Crossley Bros., Ltd.) Mr. J. Crinion (Card and Blowing Room Operators), Sir V. Caillard (Vickers, Ltd.), Mr. B. Cooper (Cigar Makers), Mr. C. Coleing (Drapers' Chamber of Commerce), Mr. F. D. Docker, C.B. (President of the Federation of British Industries), Sir A. Firth, Bart. (Firth and Sons, Ltd.), Mr. F. Gilbertson (Pontardawe Steel, Tinplate, and Galvanising Works), Mr. I. Gwynne (Tin and Steel Mill Men's Union), Sir R. Hadfield (Hadfield, Ltd.), Mr. J. Henson (National Sailors and Firemen's Union), Mr. J. S. Hill (Engineering and Allied Trades Societies Federation), Mr. E. Manville (Daimler Co.), Mr. Mallalieu (Felt Hatters' Union), Mr. H. H. Marshall (Marshall and Sons), Mr. W. Mullin (Card and Blowing Room Operatives), Mr. F. Moore (Moore, Eady, and Murcott Goode), Mr. R. T. Nugent (Federation of British Industries), Mr. Arthur Pugh (British Steel Smelters' and Kindred Trades' Association), Sir H. Rogers (Birmingham Small Arms Company), Mr. J. Taylor (Midland Trades Council), Mr. A. Todd (Iron Founders' Friendly Society), Mr. V. H. Smith (Gloucester Railway Carriage and Waggon Co.), Mr. J. H. Wilson (National Seamen's and Firemen's Union), and Mr. W. J. Davis (Brass Workers and Metal Mechanics).

A Position of Gravity.

The Chairman referred to the gravity of the prevailing unrest, not only among workmen but equally among employers and business men. It was necessary for the Alliance, he said, to strengthen and extend its organisation as rapidly as possible, so that employers and employed acting together should assist and perhaps guide the Government in the difficult and involved situation which had arisen. The constitution of the Alliance should be broad and comprehensive enough to obtain the practical co-operation of everyone associated with the industrial life of the nation. There had been a better relationship growing up between employers and employed, but he thought it had to be admitted that in a good many cases workmen had not in the past received a due proportion of the results of their industry. Employers must recognise that workmen in the future must be better paid than they had in the past, better housed, and better educated. The workman, on the other hand, must recognise that a full wage carried with it the obligation of a full day's work, and that where a full day's wage is paid interference with the productivity of industry must not be allowed. The Chairman moved the adoption of the constitution, the main objects of which are:—

* Abstract of Lecture delivered at The Royal Institute of Public Health, May 30, 1917.

To secure the active co-operation of employers and employed in the discussion and treatment of questions affecting labour and employment with the special object of securing that these should be dealt with before they have reached the stage of acute controversy. To promote generally the welfare of the industrial workers of the country and the efficiency of its industries. To arrange in conjunction with the proper Departments of the Government, as one of the most urgent problems, for the reinstatement in civil employment at the end of the war of men serving with the forces and munition workers. A resolution was also passed urging the Government to abstain in future from action affecting the conditions of manufacture and employment until the joint advice of employers and employed has been obtained, and from interference in industrial disputes until every form of direct negotiation had been exhausted.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, May 3, 1917.

Prof. W. J. POPE, M.A., D.Sc., F.R.S., President,
in the Chair.

THE PRESIDENT referred to the loss sustained by the Society, through death, of the following Fellows:—Arthur Edwin Tate (died of wounds), Benjamin Horatio Paul, John Flraid Richardson, and Francis Sutton.

Certificates were read for the first time in favour of Arthur John Daly, B.Sc., 67, Albyn Road, St. John's, S.E. 8; Frederic William Gamble, White Gables, Kenton Lane, Harrow; Henry James Hinks, 38, Burford Gardens, Palmer's Green, N. 13; Louis Frederick William Leese, Matillas, Guadalajara, Spain; Herbert Skellon, R.Sc.; Newlands, Water Street, Leyland; Nicholas Karrachy Smith, B.Sc., 254, Barcombe Avenue, Streatham Hill, S.W.

Messrs. R. R. Baxter and H. H. Hughes were elected Scrutators, and a ballot for the election of Fellows was held. The following were subsequently declared duly elected as Fellows:—John Anderson, M.A., B.Sc.; Charles Claude Carpenter; Beni Madhub Chakravarti, B.A.; Herbert Edwin Course; Percy Cowell; Charles Kilner Crosland; Kenneth Shallcross Dickinson; Gordon Harvey Field; William Geary; Leon Daniel Goldsmith, B.Sc.; Harold Pearson Hird; Alfred Bishop Hitchens, A.M., Ph.D.; Arthur Charles Hoare; Tom Macindoe McKenzie; George Samuel Mason, B.Sc.; William Mather, B.A.; John Calvert Oxley; Leonard Roger Batten Pearce, B.Sc.; Sydney Albert Pearman, B.Sc.; Alfred George Pollard, B.Sc.; William Hyman Prince; George Reeves, B.Sc.; George Robertson, M.A., B.Sc.; Ernest Harry Rodd, D.Sc.; Oge Roewade; William Smith, B.Sc.; Robert Stevenson; James Netherwood Sugden, B.Sc.; Vetscheslav Evgenievitch Tschtschenko; Harold Waterland; Hugh Edmund Watts, B.Sc., Ph.D.; Arthur Worthington.

The following papers were read:—

"Researches on Asymmetric Nitrogen Compounds. Part III. Hydroxyphenylglycine." By the late R. MELDOLA, H. S. FOSTER, and R. BRIGHTMAN.

"Researches on Asymmetric Nitrogen Compounds. Part II. Some Nitrated Hydroxydiphenylamines." By the late R. MELDOLA, H. S. FOSTER, and R. BRIGHTMAN.

"Researches on Asymmetric Nitrogen Compounds. Part III. Hydroxyphenylglycine." By the late R. MELDOLA, H. S. FOSTER, and R. BRIGHTMAN.

"Contributions to the Chemistry of Caramel. Part I. Caramelan." By Miss M. CUNNINGHAM and C. DORÉ.

Ordinary Meeting, May 17, 1917.

Prof. W. J. POPE, M.A., D.Sc., F.R.S., President,
in the Chair.

THE PRESIDENT referred to the loss sustained by the Society, through death, of:—Norman Phillips Campbell (killed), George Stanley Cooper, and Peter MacEwan.

THE PRESIDENT announced that in view of the need for economy in the use of paper the Council had decided not to publish in 1917 the usual list of Fellows.

Messrs. J. N. Sugden, J. E. Dunstan, W. Smith., S. P. Kipping, L. R. B. Pearce, S. F. Garrard, and H. J. Cross were formally admitted Fellows of the Chemical Society.

Certificates were read for the first time in favour of Montague Aldridge, M.A., Cranleigh School, Surrey; Carleton Ellis, 143, Gates Avenue, Montclair, N.J., U.S.A.; Hubert Henry Hazel, B.A., Caradoc, Balmoral Road, Parkstone, Dorset; Albert Edward Mills, Ashton House, Oldfield Park, Bath; Leslie O'Brien, 109, Leopold Road, Edge Lane, Liverpool; Herbert Swann, B.Sc., 47, Upper Wickham Lane, Welling; Michael J. Walsh, M.Sc., Continuous Reaction Co., Ltd., Church Road, Batterssea, S.W. 11; Percy Noel Williams, B.Sc., 73, Bexley Road, Erith.

The following papers were read:—

"Studies on the Walden Inversion. Part VI. The Influence of the Solvent on the Sign of the Product in the Conversion of Phenylbromoacetic Acid to Phenylamino-acetic Acid." By G. SENTER and S. H. TUCKER.

"An Apparatus for the Reduction of Volumes of Gases to Standard Temperature and Pressure." By A. V. C. FENBY.

"The Detection of Traces of Mercury Salts for Toxicological Purposes." By K. C. BROWNING.

SOCIETY OF GLASS TECHNOLOGY.

Ordinary Meeting, May 16, 1917.

Mr. A. S. ESSLEMONT, Vice-President, in the Chair.

AT the invitation of the Council of the Institute of Chemistry the meeting was held in the rooms of the Institute, Russell Square, London.

After the formal business had been dismissed the Chairman called upon Prof. Herbert Jackson, F.R.S., F.I.C., to address the meeting, at the same time offering him the congratulations of the Society on his being made a Fellow of the Royal Society. These congratulations were singularly appropriate when it was remembered that the honour had been the outcome largely of the Professor's classical work in the domain of glass research.

Prof. JACKSON was received with acclamation, and after bidding the Society welcome in the name of the Institute of Chemistry, gave a succinct account of the wonderful work accomplished in glass research since 1914 at the instigation of the Institute and the Ministry of Munitions. One outcome of that work had been the placing of at least fifty new batch formulæ at the disposal of glass manufacturers, to experiment with, to adopt, and to improve. Amongst the most important formulæ available could be mentioned batches for: (1) Resistant and ordinary chemical ware; (2) Soft glass for lamp work; (3) Combustion tubing; (4) Various types of glasses for X-ray work; (5) Opal glasses; (6) Thermometer glasses; (7) Optical glasses. To show the widespread nature of the researches already carried out upon glass, the effect of almost every known element had been tried, and many glasses with interesting properties were now available both for present and post-war use.

Continuing his address, the speaker complimented glass manufacturers upon the success which had attended their efforts and spoke of the deep debt of gratitude which the country owes them. By fostering research in many direc-

tions, and by the admission of science in its most advanced form into their industry they had ensured its progress in the future. The enthusiasm of the manufacturer was reflected in the founding of a strong Society of Glass Technology, and the interests of the glass industry at large were being well served by the Glass Technology Department of the University of Sheffield and by the numerous representative committees set up by the Ministry of Munitions. The outlook for the future was most encouraging and promising, for numerous interesting problems were needing attention, whilst new ideas and new methods all required testing. The glass industry was a striking example of the co-ordination of the manufacturer and scientist at its best.

The professor then passed on to a most instructive discourse upon the properties of glass, dealing first of all with the relation between hardness and temperature of founding and leading up to brittleness and the amorphous nature of glass. The causes of crystallisation were pointed out, and the analogy between well-known crystallisation phenomena in pure chemistry and in actual glass manufacture was emphasised. In particular the necessity for homogeneity was commented upon. Given good homogeneity, many of the problems of annealing and faulty metal would automatically disappear. A most instructive lecture was concluded by the recounting of many new facts dealing with opal glasses and colour in glass, whilst lines on which research could be carried out were indicated. Not the least pleasing feature of the lecture was the telling way in which the interdependence of science and industry was demonstrated, and members of the Society would always appreciate the limning of the science and art of an old and beautiful industry by a master of his craft.

Prior to the above meeting, the members of the Society paid a most enjoyable visit to the works and showrooms of Messrs. Powell and Sons, Ltd., Whitefriars.

The next meeting of the Society will be in June at the University, Sheffield, when a joint discussion on refractory materials has been arranged with the Faraday Society.

NOTICES OF BOOKS.

The British Journal Photographic Almanac, 1917
Edited by GEORGE E. BROWN, F.I.C. London: Henry Greenwood and Co., Ltd. Pp. 779. Price 1s. net.

THE text of the issue of the Photographic Annual for 1917 has had to be somewhat restricted, and the space given to advertisements also, partly owing to the shortage of paper; but most of the usual features have been retained, and the Annual remains a very useful guide for both professional and amateur photographers. An epitome of progress for the year is provided, and a large amount of useful miscellaneous information, such as formulæ, exposure tables, optical tables, &c., is to be found in the book.

A Short System of Qualitative Analysis. By R. M. CAVEN, D.Sc. (Lond.), F.I.C. London, Glasgow, and Bombay: Blackie and Son, Ltd. 1917. Pp. viii+162. Price 2s.

THIS book is an abridgment of the author's "Systematic Qualitative Analysis," and contains a very useful first course in inorganic analytical work which would give the student a thorough grounding in its principles and practice. The first part deals with the general theory of analysis, and explains the application of reactions in the dry way, the general properties and reactions of substances in solution, and the system of the classification of metallic and acid radicals adopted. In the second and practical part of the book the reactions of the most important ions are described in detail, with tables of separation, and finally a complete scheme for the analysis of a mixture is given. The text is full and complete as far as it goes, and the student is

always encouraged to do his work thoughtfully and exercise his reasoning power as much as his memory in doing analytical work.

The Chemists' Year Book, 1917. Edited by F. W. ATTACK, M.Sc. (Tech), (Manch.), B.Sc. (Lond.), F.I.C., assisted by L. WHINGATES, Assoc.M.S.T. in Two Volumes. Third Edition. London and Manchester: Sherratt and Hughes. 1917. Pp. 62+1030. Price 10s. 6d. net.

CONSIDERABLE alteration has been made in some sections of the third edition of this handbook, while the article on "Textile Fibres" has been entirely rewritten. New sections on the analysis of essential oils, efficiency boiler plant, cement, and paints and pigments have been added, and all the data have been carefully revised. The handbook contains a great number of tables, giving numerical data of all kinds and physical constants, and it also contains complete directions for qualitative analysis and for many processes of technical analysis. It is a possession which every chemist will value as being full of information in a conveniently arranged form, and at a very moderate price in view of its comprehensiveness.

The Tutorial Chemistry. Part II. *Metals and Physical Chemistry*. By G. H. BAILEY, D.Sc. (Lond.), Ph.D. (Heidelberg). Edited by WILLIAM BRIGGS, LL.D., M.A., B.Sc., F.C.S. Third Edition. London: University Tutorial Press, Ltd. 1917. Pp. viii+460. Price 4s. 6d. net.

THE second part of the "Tutorial Chemistry," the third edition of which has just been published, deals with the elements of physical chemistry, and of the study of the metals, and is already well known as a very useful if not indispensable text-book for students who hope to become candidates for the Intermediate Science Examination of London University. It is specially valuable for those whose time of preparation is short, and who therefore require very careful guidance as to the exact scope of the syllabus. The reader who studies the book thoroughly and gets a real grasp of its subject matter will certainly have very little to fear when the day of examination arrives. The book provides a complete course of inorganic chemistry, with practical work and sets of well-chosen questions on each chapter. The section on physical chemistry has been considerably extended, and the whole text has been thoroughly revised in the new edition, while the chapter on Crystallisation and Crystallography has been transferred to an appendix to make room for new matter.

CORRESPONDENCE.

THE ELECTRO-THERMAL POSITION OF BORON.

To the Editor of the Chemical News.

SIR,—When some time ago my theoretical papers on thermal chemistry appeared in the CHEMICAL NEWS, I pursued the theoretical investigation much further, intending an experimental proof of the views suggested therein.

The revision of the thermal data then extant suggested the element boron as likely in its combinations to be suitable for such an investigation.

Taking the matter up again I find that Mellor in his "Inorganic Chemistry" gives an electro-chemical position to boron in the electro-chemical scale of the elements, and would call the attention of readers of the CHEMICAL NEWS to an electro-thermal consideration of the elements, more particularly in their thermal relations.—I am, &c.,

J. C. THOMLINSON, B.Sc.

BRITISH PATENTS.

To the Editor of the Chemical News.

SIR,—It is a very long time since an English patent was issued by the then English Patent Office somewhere towards the end of the first half of last century, yet I am told by the Rip Van Winkle Publication Committee of the Society of Chemical Industry that all British Patents are still registered as English Patents! Carnegie would be quite safe in staking all his fortune that not a single English patent ever will, or has been, valid in either Scotland or Ireland. It seems to me that the great men on this Publication Committee are mere figureheads, and what the great men on the Council do I do not know. I absolutely refuse to believe that such men have lent their names to the wilful mutilation of the proper description of His Majesty's Royal Warrants, viz., His Majesty's Royal Letters Patent, ever since the Society was founded. Yet there it is on the face of it in black and white in their journals. This mutilated description restricts the territory of an English patentee to England; his patent is invalid in Scotland and Ireland. And the territory of a Scottish patentee is similarly restricted. The patentee cannot exercise his patent in the land of his birth. The territory of an Irish patentee is similarly restricted. He can neither use his own patent in Ireland nor in Scotland. Here is a gross abuse and manifest injustice of many years standing, absolutely staring the recently formed Association of British Chemical Manufacturers right in the face, and yet it takes no action, and it has devolved upon me to do so, with the result given at the beginning of this letter, dust thrown in my eyes. Prevarication of a bad type. It is the bounden duty of the above British Chemical Manufacturers' Association to demand that the true description of the British patents of British chemical manufacturers be mutilated no longer. I have been waiting for this Association to show its *raison d'être*. Here is such a one ready-made.

I can hardly imagine Sir Chas. Bedford saying to a Canadian chemical manufacturer, "We shall be so glad to help you in securing a British patent, and I am sure you will not mind if the little Englanders of the Society of Chemical Industry call it an "English" patent. It is just their pretty ways, and really they are very nice fellows."—I am, &c.,

JOHN GEDDES MCINTOSH.

9, Parsonage Street, E. 14.

P.S.—The Comptroller of British Patents looks on complacently at this gross abuse being perpetrated right under his nose, and merely acknowledges receipt of my letter of protest.—J. G. M.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clxiv., No. 15, April 10, 1917; No. 16, April 16, 1917.

These numbers contain no chemical matter.

No. 17, April 23, 1917.

Neutral and Acid Sulphates of Sodium.—Paul Pascal.—The author has studied the equilibrium of the ternary system, $\text{H}_2\text{SO}_4\text{—Na}_2\text{SO}_4\text{—H}_2\text{O}$, between -45° and $+210^\circ$, and the results are represented in a diagram in trilinear projection. The existence of the following compounds is indicated:— NaSO_4 , $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, $\text{Na}_2\text{SO}_4 \cdot \text{NaHSO}_4$, $\text{NaHSO}_4 \cdot \text{H}_2\text{O}$, NaHSO_4 .

$\text{NaHSO}_4 \cdot \text{H}_2\text{SO}_4 \cdot 1.5\text{H}_2\text{O}$, $\text{NaHSO}_4 \cdot \text{H}_2\text{SO}_4$. All these compounds, with the exception of the bisulphate and $\text{NaHSO}_4 \cdot \text{H}_2\text{SO}_4$, decompose when heated.

The Zirconyl Radical, ZrO .—Ed. Chauvenet.—Measurements of the hydrolysis of zirconium sulphate and chloride and determinations of the conductivity show the existence of the zirconyl radical, and the freezing point of a solution of $\text{ZrCl}_4 + 2\text{NaOH}$ is practically the same as that of a solution of $\text{ZrOCl}_2 + 2\text{NaCl}$ of the same concentration. Thermochemical experiments confirm the existence of this radical in zirconium compounds.

Isomerisation by Migration of the Double Bond in Ethylenic Acids. $\alpha\beta$ -Phenylcrotonic Acid, $\text{C}_6\text{H}_5 \cdot \text{CH}_2 \cdot \text{CH} = \text{CH} \cdot \text{CO}_2\text{H}$.—J. Bougault.—The action of boiling alkalis is supposed to transform the $\beta\gamma$ -ethylenic acids into the $\alpha\beta$ -compounds, but as a matter of fact the reaction is reversible, although the point of equilibrium is usually very near the total transformation into the $\alpha\beta$ -acids. The author has proved experimentally the reversibility of the reaction.

MISCELLANEOUS.

Modern Volumetric Analysis.—In the estimation of iron potassium bichromate standard solutions are often used, when as it is better to give every precaution to any incidental reoxidation when titrating with the reagent; in my own case the simpler formulae deducible from the solution of zinc in hydrochloric acid prevent any doubt as to the use of the other method of reducing with tin and hydrochloric acid mentioned in Sutton's "Volumetric Analysis" as being other than cumbersome.—J. C. THOMLINSON.

Royal Institution.—A General Meeting of the Members of the Royal Institution was held on the 4th inst., the Duke of Northumberland, K.G., President, in the Chair. Mrs. Harriman Dickinson, Alfred Dobree, and Mrs. Florence Stacpoole were elected Members. The Special Thanks of the Members were returned to Prof. Frank Clowes, D.Sc., for his Gift of a Print by Gilray, showing Dr. Garnett, with the aid of his Assistant, Humphry Davy, lecturing at the Royal Institution.

John Wheldon and Co.'s Chemical Catalogue.—Messrs. John Wheldon and Co., of 38, Great Queen Street, Kingsway, W.C. 2, have recently purchased the library of the late Dr. Hugo Müller, F.R.S., and have published a catalogue containing details of over 500 of the books comprising it, and of other purchases. Many complete sets of scientific periodicals are included in the list, and some valuable standard works. One interesting item is a copy of Boyle's "Opera Varia" which was published in 1677, while many new text-books and educational works are to be found in the list, which also contains a number of classical German works. The sale of Dr. Müller's library provides scientific men with an opportunity of obtaining some interesting old books, as well as a considerable number of modern ones at a reduced price, and a copy of the catalogue will be found well worth the trouble of writing for it.

MEETINGS FOR THE WEEK.

MONDAY, 11th.—Biochemical Society, 5.30. "Occurrence of the Fat-soluble Accessory Substance in certain Animal and Vegetable Fats," by J. C. Drummond. "Bi-hydrocholesterol and its Oxidation Products," by G. W. Ellis and J. A. Gardner. "The Composition of the Unassimilable Matter of Human Faeces," by J. A. Gardner. "Cholesterol Metabolism," by J. A. Gardner and Callier.

THE CHEMICAL NEWS

VOL. CXV., No. 3003.

THE MOLECULAR REFRACTIVITIES OF CERTAIN ELEMENTS AND SIMPLE COMPOUNDS.

By GERVAISE LE BAS.

THE author showed in 1907 that at the critical and boiling points and, under corresponding pressures, the molecular volumes and molecular refractivities of the *n* paraffins are proportional to each other (*Phil. Mag.*, 1907, [6], xiv., 324).

It has also been shown that both of these physical constants are subject to the 4:1 rule, which connects the volumes of carbon and hydrogen in compounds. This relation is similar to the one existing between the valencies of these atoms.

Traube has also followed this relation in a number of organic series from a study of the refractivities, and has also shown that the valency rule applies to oxygen, nitrogen, and a number of other atoms (*Ber.*, 1907, xl., 1, 130).

The stere value which the writer calculated was—

$$r_a(H) = 0.780.$$

This has been found, from a study of inorganic and organic compounds, to be exactly a third of the volume of hydrogen at absolute zero:—

$$V_a(-273) = 3 \times 0.780 \\ = 2.340$$

Traube extended his study to the refractivities of the elements and certain simple compounds in the gaseous state by an application of the stere value 0.787. This value has been found to be inaccurate, since the results show only an approximate adherence to the valency rule. Moreover, a number of important facts seem to have been lost sight of.

The value of the unit is obtained from an examination of the oxides of carbon:—

	C : O.	Δ .	O : C : O.
R_a	5.03	1.68	6.71
O''	1.68	2×0.84	$2O''$ 3.36
C :	3.35		C : 3.35
	4×0.84		4×0.84

The relations of carbon and oxygen are thus almost exactly 4:2, the stere value of the unit being evidently 0.84, which is the refractivity of hydrogen under the conditions.

This is proved from an examination of methane,—

$$R_a(CH_4) 6.61 = 8 \times 0.83.$$

OXYGEN COMPOUNDS.

	O : O	H > O : O < H	H > O : O
Free oxygen.		Water.	Hydrogen peroxide.
	4.08	7.64	5.93
	5×0.82	9×0.85	7×0.85

It is observed that the combinations <O:O> or >O:O< show an augmentation of one unit, which is considered to be due to unsaturation. This is not shown in the oxides of carbon, the reason being that in the above

three cases there is an unsaturated linkage between two similar atoms. In the former case the oxygen atoms are separated by carbon. It results that any excess is thrown on to the carbon, as it should be in the carbonyl, carboxyl, and other similar groups. The carbon then equals four times the refractivity of hydrogen.

A parallel case is that of the ethenoid group, which in the liquid state shows an augmentation of $1.54 = 2 \times 0.77$, or 2H.

The rule thus seems to be—When there is a union (:) between two similar atoms there is an augmentation of the refractivity; when the atoms are dissimilar the refractivities of the atoms are the same as when singly linked. The real atomic refraction of carbon is thus in liquids 3.12 (4×0.780), and not 2.50 or 3.40 in gases.

It is important to notice that not only is the complexity of the vapour of water shown to be $2H_2O$, but also that the formula is similar to that of ethylene, and is unsaturated.

This value of the association factor $x = 2$ is confirmed by a study of the specific cohesion and capillarity.

Specific cohesion (Walden)	$x = 1.98$
Capillarity (Ramsay and Shields)	$= 2.60$

The two alternative formulæ of hydrogen peroxide—

HO : OH	H ₂ O : O
Symmetrical.	Unsymmetrical

There is an augmentation of one unit only in the case of :O, not in that of :O. For this reason hydrogen peroxide is thought to be unsymmetrical.

NITROGEN COMPOUNDS.

Free nitrogen, in contrast to the other elements, shows a diminution of the refractivity,—

	N : N.
R_a	1.41
6×0.85	5.10
Δ	-0.69

Nitrogen, like oxygen, is unsaturated, but in the opposite sense. Compounds with the linkage N:N, on the other hand, show augmentations.

	H > N : N < H	H > N - N < H
	Ammonia.	Hydrazine (liq.)
R_a	11.26	8.33
12×0.85	10.20	10×0.85 .. 8.50
Δ	+ 1.06	—
	H > HO : N : N < OH	N > O
		7.58
	R_a 14.38.	
	17×0.85 .. 14.45	9×0.85 .. 7.65

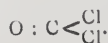
All of the above unsaturated compounds possess augmented refractivities to the extent of one unit, 0.85. Moreover, they show two similar atoms united as in ethylene. The above formulæ are thus indicated by the refractivities of the compounds.

For N : O, on the other hand, it is found that —

$$5 \times 0.85 = 4.25. \quad R_a 4.46. \quad \Delta +0.21$$

The following compounds are normal:—

H.C : N	N : C - C : N
R_a 6.63	11.98
8×0.83	14×0.855



R _a	17.32
C : O	5.03
2Cl	12.28 (2 × 6.14)

Enr _a	17.31
R _a	17.32

Free hydrogen shows evidence of unsaturation.

H—H	ΣH _a 1.70	R _a 2.08	Δ +0.38
H—Cl	ΣH _a 6.63	6.68	—

The most important points to notice in this paper are :—

- (a) The value of the unit is 0.85 for gases.
 (b) The relative refractivities are C = 4HO = 2H,
 N = 3HCl = 7H.
 (c) The unsaturation of such groups as—

O : O, N : N, C : C, H : H.

is such as to indicate an augmentation of one unit.

(d) The evidence in favour of association and of the degree of association in some of the compounds with the formulæ of such substances as water and ammonia. Water and ammonia are unsaturated, whilst the formula of hydrogen peroxide is the unsymmetrical one.

SOME MAIN LINES OF ADVANCE IN THE DOMAIN OF MODERN ANALYTICAL CHEMISTRY.*

By A. CHASTON CHAPMAN.

(Concluded from p. 271).

I HAVE now touched on a few of the main lines along which analytical chemistry has advanced during recent years, and have endeavoured to show that, so far from being the exhausted and lethargic handmaiden, it is, in fact, as alive, as progressive, and as originative of research as any other branch of our science. That this is not always fully realised, and that there has been—and is even now in some quarters—a tendency to regard analytical chemistry merely as a useful art and its practitioners as highly skilled labourers, is unhappily the case. That there are here and there a few analysts to whom that description might be correctly applied is undoubtedly true, but the same is, of course, equally true of the medical and other professions.

The analytical chemist of to day is, in fact, being continually faced with new problems that frequently demand for their solution the possession in a high degree of those special qualities of intellect and character which go to make the successful investigator in the domain of pure chemical science. For many chemical consultants life is a continuous series of technical problems, and I am not indulging in any exaggerated language when I say that the really successful consulting and analytical chemist must not only have a good general scientific training, an extensive knowledge of general chemistry, and a genuine love of his work, but he must be mentally alert and adaptable and possess the aptitude for research in a high degree.

With regard to the teaching of analytical chemistry, there is much that I should like to say if time permitted, and in particular I should like to plead again for the establishment in our universities and university colleges of chairs of analytical chemistry. I have already dealt with this subject at some length in an address to another society, and perhaps I may be allowed, in concluding, to quote the following remarks from that address :—

"Having very briefly touched on the nature and extent of the scientific equipment needed for the successful practice of analytical chemistry, we may reasonably inquire

whether the training which our young professional chemist^s obtain is such as is calculated to insure the best results. Whilst there may possibly be some difference of opinion as to the precise position which a study of chemical analysis should take in the training of the chemical teacher, there can surely be none as to its supreme importance in the training of the professional chemist. In the great majority of cases it is the actual instrument by which, directly or indirectly, he is to earn his livelihood, and in every case it must tend to produce (if properly taught as a living subject and not as a mass of tedious prescriptions and formulas) a deeper insight into the nature of chemical reactions, an appreciation of the influence of mass and other disturbing factors, and a recognition of the importance of attention to minute detail. In addition to this, it affords endless opportunity for the acquirement of dexterity in constructing and manipulating scientific appliances, and in all these ways renders invaluable service in the making of the successful technical chemist. Now, if all this be true—and I do not see how it can be denied—analytical chemistry ought clearly to take an outstanding position in our universities and university colleges, as it is from them that, more often than not, the young chemist proceeds directly to the practice of his profession. Unfortunately, the position which it takes in those institutions is not, as a rule, a high one, nor one at all commensurate with its importance. I believe I am correct in saying that in no university in this country does a chair of analytical chemistry exist, and that a subject which is admittedly of such great importance is entrusted to teachers who, however well qualified and capable they may be, have, as a rule, to teach it, if I may use the expression, incidentally.

"So large a subject, and one which is in constant process of development, might well, it seems to me, be entrusted to a specially appointed professor, who would have the opportunity of keeping himself fully abreast of the developments of his subject, and who would have the time to deal with it in a manner practically impossible under the existing conditions. Such chairs of analytical chemistry exist in very many of the more important American and Continental universities, and it can scarcely be contended that what has been found desirable in so many other parts of the civilised world is unnecessary in Great Britain. Chairs of analytical chemistry, for example, exist in Yale, Virginia, Johns Hopkins, Cornell, and Columbia Universities, to name only those of which I know, and I believe I am correct in saying that in Columbia University there are no fewer than three such professors. In many of the university prospectuses great emphasis is laid on the importance of analytical chemistry, and from one of the Yale calendars I cannot refrain from quoting the following words : 'There is probably no branch of chemical study as important as qualitative analysis in its use in developing the reasoning faculties and enabling the student to generalise and to classify chemical phenomena.' In Heidelberg, Munich, Leipzig, Würzburg, and other German universities, in the Imperial technical high schools at Stuttgart, Vienna, and elsewhere, such chairs exist, as well as at Upsala, in most of the Swiss and Belgian universities, and in some of the Italian. In regard to France and one or two other countries I have no definite information, but I think I have said enough to establish my point—that in many of the world's leading universities the teaching of analytical chemistry is entrusted to a specially appointed professor, who takes equal academic rank with his other chemical colleagues. Even when this is not the case, assistant professors or special assistants are frequently appointed to deal solely with this branch of chemistry. It clearly cannot be objected that it has not been our custom in this country to appoint professors to deal with special branches of chemistry, since in some of our colleges chairs exist devoted to physical chemistry, biochemistry, tinctorial chemistry, fuel chemistry, brewing chemistry, agricultural chemistry, technical chemistry, and metallurgy.

* A Lecture delivered before the Chemical Society, March 15, 1917.

"I am not foolish enough to imagine that the establishment of chairs of analytical chemistry in all or any of our universities and colleges would bring forth a new heaven or a new earth, but at least it is certain that this highly important branch of chemistry would be taught under better conditions than those which in many cases exist at present. The teachers, being in a position to devote themselves entirely to their special branch of instruction, would be able to give more time and attention to the student, and surely in no branch of chemistry is close and constant supervision of practical work so necessary. They would also have the time to make themselves thoroughly conversant with their subject in both its theoretical and practical aspects, as well as to keep in touch with modern developments, and their laboratories might even become in process of time centres of original work in a department of our science in which research has been for so long neglected."

Since the above was written, some signs of progress auguring well for the future have been observable. That analytical chemistry is in a condition of vigorous growth I have endeavoured to show, and that it may continue to flourish exceedingly must be the earnest wish of every member of this society. All the branches of our science are reciprocally reactive and closely interdependent, and on the progress of British chemistry as a whole, and on the position which it holds in the national esteem, the future of this country, and indeed of the Empire itself, will to no small extent depend. May our rulers and our people be wiser in the future than they have been in the past.

A SPECIFIC GRAVITY BALANCE FOR GASES.*

By JUNIUS DAVID EDWARDS.

THE need for an accurate method of determining gas densities has been especially urgent in the natural gas industry where the measurement of gas by means of orifice meters requires a knowledge of the density of the gas. An investigation by this Bureau of the effusion type of apparatus, which has been generally used for this purpose, but which has proven unreliable in practice, has shown the need of more precise methods. To supply this need the present method was adopted, and suitable apparatus designed.

The principle of the method employed is based upon the laws of the compressibility (Boyle's law) and the buoyant effect of gas. The balance contains a beam which carries on one end a relatively large globe, and on the other a small counterweight; the beam is enclosed in a gas-tight chamber. The buoyant force exerted upon the globe is proportional to the density of the gas, and therefore to its pressure. Therefore if the buoyant force exerted upon the globe is made the same as shown by its position of equilibrium when it is suspended successively in two different gases, then the densities of the two gases must be the same at these pressures, or the specific gravity is the inverse ratio of the pressures.

In operation the balance-case is filled with air and the pressure adjusted until the beam balances. It is then filled with gas, and the pressure required to secure a balance is determined in the same way.

The apparatus described provides a quick accurate means of determining gas density. The balance beam is supported on two needle-points which give high sensibility. The needles are easily adjustable, and in contrast with the metal or quartz knife-edge usually used, can be obtained almost anywhere, are inexpensive, and can be replaced as often as necessary. The success obtained in the use of this apparatus is mainly due to the high sensibility afforded by this means of support. It is necessary to remove the beam from the case only when it is desired to

transport it. No levelling bottle is necessary in adjusting the gas pressure within the balance, this being accomplished by means of a needle valve which affords precise control. A portable outfit is described which combines lightness of weight, convenience in use, and durability without any great sacrifice of accuracy. No preliminary calibration of the apparatus is necessary. The results obtained with this balance were compared with those obtained by a direct weighing method, and it was shown that an accuracy of 1 or 2 parts per 1000 could be obtained quickly and without elaborate precautions.—*Journal of the Franklin Institute*, clxxxiii., No. 3.

THE TRANSFORMATION OF NITRILES INTO AMIDES BY HYDROGEN PEROXIDES.

By L. McMASTER and F. B. LANGRECK.

THE first use made of hydrogen peroxide as a hydrolytic agent for converting nitriles into amides was by Radziszewski (*Ber.*, 1885, xviii., 355). The action takes place according to the equation: $\text{RCN} + 2\text{H}_2\text{O}_2 = \text{RCONH}_2 + \text{H}_2\text{O} + \text{O}_2$.

Radziszewski found that the reaction took place easily in the presence of a small amount of alkali and at a temperature of about 40°. He was of the opinion that it would proceed especially well in all cases where the amide formed is insoluble in water, and gave as examples the formation of benzamide from benzonitrile and capronamide from capronitrile. Radziszewski used a 3 per cent solution of hydrogen peroxide.

Deinert (*Journ. Prakt. Chem.*, 1895, [2], lii., 431) applied this method to different nitriles, and obtained very fair yields of the corresponding amides from benzonitrile and *p*-tolunitrile, poor yields from benzyl cyanide and *β*-naphthonitrile, very poor yields from propionitrile and *α*-naphthonitrile, and no yield at all from *o*-tolunitrile. He thus came to the conclusion that the nitriles gave different results according to their constitution.

Bogert and Hand (*Journ. Am. Chem. Soc.*, 1902, xxiv., 1034, and following papers) used this same method for the direct formation of quinazolines from *o*-acylaminobenzonitriles, and Bogert and his associates have frequently used the same method since.

Keiser and McMaster made use of this method to convert fumarnitrile into fumaramide (*Am. Chem. Journ.*, 1913, xlix., 81). Practically a quantitative yield was obtained.

In October, 1915, we began a more thorough study of this method to see whether it could not be made of wider application and better yields obtained, particularly by the use of more concentrated solutions of hydrogen peroxide than had been previously used. Deinert used 1.8, 2.5, and 8.0 per cent solutions, but found that the 2.5 per cent solution was the best one to use. We have applied our modification of the method to the transformation of benzonitrile, *m*-nitrobenzonitrile, *o*-tolunitrile, *p*-tolunitrile, *α*-naphthonitrile, *β*-naphthonitrile, terephthalitrile, trichloroacetoneitrile, and isobutylacetoneitrile into the corresponding amides. Recent abstracts give an account of some recent work by Dubsky (*Journ. Soc. Chem. Ind.*, 1916, xxxv., 829; *Journ. Chem. Soc.*, 1916, [I.], cx., 550; from *Journ. Prakt. Chem.*, 1916, [2], xciii., 137) on the transformation of nitriles into amides by the Radziszewski method. Dubsky has brought about the hydrolysis of several nitriles into amides by using a large excess of a 3 per cent solution of hydrogen peroxide. He was thus able to convert *o*-tolunitrile and *α*-naphthonitrile into amides, whereas Deinert found that they remained practically unchanged when treated with the usual amount of hydrogen peroxide.

We have been unable to obtain the original article of Dubsky's, and since we have worked with two of the same nitriles mentioned in the abstracts and found that the same results were obtained by using concentrated solutions of the peroxide instead of a large excess of the usual 3 per

* Abstract of Technologic Paper No. 89, U.S. Bureau of Standards.

cent solution, and since we have applied the method to a larger number of cases than Dubsky has, we thought that we should publish our results already obtained with the nitriles mentioned above. We also intend to apply the method in the case of many other nitriles.

Experimental.

Benzonitrile.—Five grms. of benzonitrile were added to 50 cc. of a 6 per cent solution of hydrogen peroxide, and the mixture made slightly alkaline with sodium hydroxide. The mixture was stirred at a rather high rate of speed by means of a motor-driven apparatus to insure an intimate mixture of the substances. The temperature of the mixture was kept at 65° for 1.5 hours, during which time the amide separated out as white flakes. The stirring was now interrupted, and the mixture surrounded by ice and salt, whereupon more of the amide separated. It was filtered off, washed with cold water, dried over sulphuric acid for forty-eight hours, and crystallised from absolute ethyl alcohol. The yield was about 92 per cent of the theory. *M.p.* 128°. The *m.p.* recorded in the literature is 128° (Schiff and Tassinari, *Ber.*, 1877, x., 1785).

Calculated for $C_6H_5CONH_2$ —11.59 per cent; found—11.50 per cent N.

m-Nitrobenzonitrile.—One gm. of *m*-nitrobenzonitrile was added to 15 cc. of an approximately 20 per cent solution of hydrogen peroxide, the mixture made slightly alkaline, and warmed to 65°. The mixture was shaken vigorously, placed in the dark, and allowed to stand, with occasional shaking, for twenty-four hours. At the end of one hour a thin layer of white crystals formed at the surface of contact of the hydrogen peroxide solution and the nitrile which floated on the surface. The solution became a bright yellow-green in colour. At the end of twenty-four hours the pale yellow crystals, which had separated and fallen to the bottom of the tube, were filtered off, washed with cold water, and dried on a suction filter. The crystals were dissolved in a minimum amount of hot absolute ethyl alcohol, and the amide freed from any unchanged nitrile by suddenly cooling the hot alcoholic solution in a freezing mixture. The nitrile, being less soluble than the amide in the alcohol, crystallised out first and was filtered off. On allowing the alcohol to evaporate, the amide crystallised out. This process was repeated several times until a product of *m.p.* 141° was finally obtained. The recorded *m.p.* of *m*-nitrobenzamide is 140–142° (Reichenbach and Beilstein, *Ann.*, 1864, cxxxii., 141). The final recrystallisation yielded beautiful white needles, some of which were 4 cm. in length. The crystals of the amide formed were rather difficultly soluble in ethyl alcohol, ether, benzene, petroleum ether, and water. The yield obtained was 80 per cent of the theory.

Calculated for $C_6H_4(NO_2)CONH_2$ —16.87 per cent; found—16.97 per cent N.

o-Tolunitrile.—Deinert (*loc. cit.*) could not transform this nitrile into the corresponding amide by the use of hydrogen peroxide. Dubsky (*loc. cit.*) found that 2.5 grms. of the nitrile in 50 cc. of methyl alcohol gave a yield of 2.1 grms. of *o*-toluamide on treatment at 40–60° with 200 cc. of 3 per cent hydrogen peroxide and 10 cc. of N sodium hydroxide solution, the reaction product being neutralised, evaporated to dryness, and extracted with alcohol.

We added 10 cc. of a 15 per cent hydrogen peroxide solution to 1.1 gm. of the nitrile in a large test-tube, and, after making the mixture slightly alkaline, it was warmed to 65° and shaken vigorously. After standing twenty-four hours a white crystalline mass had formed at the surface of the liquid. On warming the mixture again the unchanged nitrile separated from the enclosing crystalline mass. The contents of the tube were again heated to 65°, shaken, and allowed to stand for another twenty-four hours, whereupon more of the amide was formed. On further similar treatment no more amide formed. The

crystals were filtered off on a suction filter, dried, and taken up in absolute ethyl alcohol. From the third recrystallisation the amide separated as white semi-transparent needles, readily soluble in ethyl alcohol, moderately soluble in ether, and quite insoluble in cold water. The crystals obtained melted at 138°. Weith found that *o*-toluamide melts at 138° (*Ber.*, 1873, vi., 42). The yield was 90 per cent of the theory.

Calculated for $C_6H_4(CH_3)CONH_2$ —10.37 per cent; found—10.42 per cent N.

p-Tolunitrile.—Deinert obtained from 2 grms. of this nitrile dissolved in alcohol, 2 grms. of amide (instead of 2.3 grms.) which melted at 155°. We added 1 gm. of the nitrile to 10 cc. of a 15 per cent solution of hydrogen peroxide, made the mixture slightly alkaline, and warmed it to 60°. The nitrile melted to a yellow oil. After shaking the mixture for some time it was allowed to stand for twenty-four hours. The amide was filtered off, dried, and crystallised from absolute ethyl alcohol. The crystals melted at 155°.

The experiment was repeated by treating 2 grms. of the nitrile with 50 cc. of a 10 per cent hydrogen peroxide solution and warming the mixture to 60°. Instead of shaking the mixture we stirred it for one hour, at the end of which time the reaction was complete. The voluminous flaky mass of amide on the surface of the liquid was filtered off, washed with water, dried, and crystallised from ethyl alcohol. The crystals were found to melt at 155°. The literature records various melting-points for *p*-toluamide. Fischli gives 151° (*Ber.*, 1879, xii., 615), Gattermann and Schmidt give 156° (*Ann.*, 1888, ccxlv., 51), while Holleman gives 158–159° (*Rec. Trav. Chim.*, vi., 78). Deinert records 155° (*loc. cit.*). The amide is described as fine needles when crystallised from alcohol (Fischli), or large plates when crystallised from water (Gattermann and Schmidt). We obtained monoclinic needles of about 5 mm. in length. The yield obtained was about 90 per cent of the theoretical.

Calculated for $C_6H_4(CH_3)CONH_2$ —10.37 per cent; found 10.30 per cent N.

a-Naphthonitrile.—Deinert observed practically no change in this nitrile when treated with hydrogen peroxide. Dubsky was able to convert it into the amide by means of a large excess of the reagent, but the abstracts of the article above referred to do not state the amount obtained. By treating 1 gm. of the nitrile with 20 cc. of 10 per cent hydrogen peroxide and making the mixture slightly alkaline we were able to obtain a 20 per cent yield after allowing the mixture to stand one week, with occasional shaking and warming. The mass which formed was filtered off, washed with cold water, and placed on a porous plate. It contained some unchanged nitrile which would probably have changed to the amide had we continued to add hydrogen peroxide and allowed the mixture to stand longer. The porous plate was placed in a water-oven and warmed to 45°. The greater portion of the unchanged nitrile (*m.p.* 36°) was absorbed by the plate, and the amide remained as white crystalline flakes. The amide was then freed from the remaining traces of nitrile by refluxing the mixture with a very small amount of ethyl alcohol and suddenly cooling it. The amide, being less soluble in alcohol than the nitrile, separates first and can be filtered off. The amide recrystallised from alcohol melted at 202°. The literature records 202° as the *m.p.* of *a*-naphthoamide (Hofmann, *Comptes Rendus*, 1868, lxi., 476; Leone, *Gazz. Chim. Ital.*, 1914, xiv., 122).

Calculated for $C_{10}H_7CONH_2$ —8.18 per cent; found—8.16 per cent N.

β-Naphthonitrile.—One gm. of *β*-naphthonitrile was added to 25 cc. of 10 per cent hydrogen peroxide solution, the mixture made alkaline and warmed to 70°. The mixture was shaken vigorously and then allowed to stand. At the end of one hour fine white needles began to form. The hydrogen peroxide decomposed very rapidly and the

solution became bright yellow in colour, later changing to bright red and finally to brown. Hydrogen peroxide was added from time to time, and after twenty-four hours the transformation seemed to be complete. The solid mass which had formed was filtered off and washed, first with water and then with alcohol, to remove any unchanged nitrile. The amide is difficultly soluble in alcohol, and remained on the filter. It was, however, recrystallised from alcohol and allowed to stand over sulphuric acid. Small rhombohedral plates of m. p. $192-193^{\circ}$ resulted. There was a slight sublimation during the determination of the melting-point. Vieth and Leone recorded 192° as the melting-point of β -naphthoamide (*Gazz. Chim. Ital.*, xiv., 123).

Calculated for $C_{10}H_7CONH_2$ —8.18 per cent; found—8.27 per cent N.

From 2 grms. of β - $C_{10}H_7CN$ Deinert obtained 0.8 gm. of β - $C_{10}H_7CONH_2$ instead of the calculated amount, 1.12 gm. From 1 gm. of the nitrile we obtained 0.9 gm. of the amide.

Terephthalnitrile—The dicyanide of terephthalic acid, purified from boiling alcohol, was treated with hydrogen peroxide solution and a small amount of alkali. The mixture was warmed to 40° , and a vigorous action took place. A white amorphous compound with a yellowish tinge formed. This was separated from any unchanged nitrile by boiling alcohol, in which the nitrile is soluble, while the amide is insoluble. Terephthalamide is insoluble in all ordinary solvents (de la Rue and Müller, *Ann.*, 1862, cxxi., 90). We found our product to be insoluble in all such solvents. The compound thus prepared melted above 250° , and gave off ammonia when treated with potassium hydroxide solution. The yield was not determined.

Calculated for $C_6H_4(CONH_2)_2$ —17.07 per cent; found—17.10 per cent N.

The amide was then boiled with alcoholic potassium hydroxide until ammonia was no longer evolved (ten hours). The alcohol was allowed to evaporate spontaneously, leaving the white salt of terephthalic acid. The salt thus formed was dissolved in water and treated with dilute hydrochloric acid, but not enough to neutralise the solution, for the free acid which would form is difficultly soluble in water. A concentrated solution of barium chloride was now added to the solution, and also more hydrochloric acid to make the mixture more nearly neutral. White barium terephthalate formed, which was washed on a suction filter and dried at $150-160^{\circ}$ for two days.

Calculated for $C_6H_4(CO_2)_2Ba$ —45.58 per cent; found—45.52 per cent Ba.

It was thus proved that we had prepared the pure terephthalamide from the nitrile.

Trichloroacetoneitrile.—Two grms. of trichloroacetoneitrile were added to 40 cc. of 3 per cent hydrogen peroxide solution. The mixture was treated with a few drops of sodium hydroxide solution and stirred at a high rate of speed for five minutes. An energetic action took place, and some free chlorine was liberated. The mixture was then set aside in the dark. At the end of two hours a few fine white needles had separated, but at the end of twenty-four hours a mass of white needles, some of which were 2 cm. in length, had separated. These were filtered off, washed with water and then with 50 per cent alcohol. The nitrile is very soluble in alcohol, while the amide is only fairly soluble in this solvent. The needle-like crystals of the amide were recrystallised from cold alcohol and placed over sulphuric acid for one week. They melted at 137° . Zincke records the m. p. as 141° (*Ber.*, 1901, xxxiii., 241).

Calculated for CCl_3CONH_2 —8.62 per cent; found—8.55 per cent N.

From 2 grms. of the nitrile we obtained 0.9 gm. of the amide.

Isobutylacetoneitrile.—One gm. of the nitrile was added to 50 cc. of 3 per cent hydrogen peroxide solution, the mixture made very slightly alkaline and stirred at a high rate of speed for one hour, the temperature being maintained at 20° . It was found in preliminary experiments that a 6 per cent or stronger solution of hydrogen peroxide caused oxidation to isocaproic acid, and the presence of even 2 or 3 cc. of a 10 per cent solution of sodium hydroxide brought about the same result. The alkalinity of the solution continually tended to disappear, and frequent additions of a drop of sodium hydroxide solution were necessary. At the end of one hour the stirring was interrupted and the mixture allowed to stand for twenty-four hours. The mixture was then cooled to 10° , when a small amount of precipitate formed. This was filtered off and crystallised from alcohol. M. p. 121° . The filtrate was evaporated to dryness on the water-bath and the residue taken up in hot absolute alcohol. On cooling the alcoholic solution flaky crystals of isobutylacetamide formed. This process was repeated several times. The crystals melted at 121° , with a slight sublimation at 118.5° . The recorded m. p. is 120° (Hofmann, *Ber.*, 1884, xvii., 1411). The yield was about 70 per cent of the theory.

Calculated for $(CH_3)_2CH(CH_2)_2CONH_2$ —12.17 per cent; found—12.22 per cent N.

Conclusions.

1. We have thus prepared nine amides in the pure condition from the corresponding nitriles. Their analyses (for nitrogen) have been made and some of their properties studied.

2. We have found that some of the nitriles, which formerly could not be transformed into amides by the ordinary concentration of hydrogen peroxide, can be transformed by more concentrated solutions of the peroxide.

3. It has been shown that the change of nitriles into corresponding amides by hydrogen peroxide, under stated conditions, is a generally applicable method.—*Journal of the American Chemical Society*, xxxix., No. 1.

ATTEMPT TO SEPARATE THE ISOTOPIC FORMS OF LEAD BY FRACTIONAL CRYSTALLISATION.

By THEODORE W. RICHARDS and NORRIS F. HALL.

ALTHOUGH the complete inseparability of isotopes by chemical means has been frequently asserted, the evidence on which this assertion is based has always seemed insufficient. The methods used have been fractional crystallisation and precipitation, but these processes have seldom been carried out more than ten times in a particular case, and frequently six or seven crystallisations have been thought a sufficiently thorough test of inseparability. A search of the literature revealed only one investigation that of Radiothorium and Thorium, by McCoy and Ross (*Journ. Am. Chem. Soc.*, 1907, xxix, 1709), where as many as 100 repetitions of a given process had been made. Thorium nitrate was dissolved in nitric acid and reprecipitated 100 times with excess of ammonia, but without change in the relative concentration of the isotopes. Precipitation with hydrogen peroxide (40 times) was also without result.

It seemed worth while, therefore, to apply to the important generalisation of Fajans, Russell, Fleck, and Soddy, a more searching test, carrying the fractionation further, and using as a criterion of success not only the measurement of radioactivity but also the determination of atomic weight.

The lead from Australian carnotite, with which the kindness of Mr. S. Radcliff and Mr. E. R. Bubb had

supplied us, and which had been used in previous atomic weight and density determinations in the Wolcott Gibbs Memorial Laboratory (Richards and Wadsworth, *Journ. Am. Chem. Soc.*, 1916, xxxviii., 1659), seemed well suited to our purpose, since its low atomic weight indicated a composition of three or four parts of the isotype (usually assumed to be radium G) to one of lead; and its β -ray activity showed that it contained sufficient radium D to serve as a basis for ionisation tests of the possible separation of this isotope from the inactive varieties. The excellent work on radium D and lead by Paneth and von Hevesy (*Sitz. d. k. Akad. Wiss. Wien*, 1913, 122, IIa, 993) had shown, indeed, that no one of the many and diverse chemical methods applied by them had effected any separation of these substances, but even here no single operation had been repeated often enough to detect the effect of exceedingly small differences in chemical or physical properties.

Preliminary Preparation of Material.

About one kilogram. of the radioactive lead was taken for this work. This included much of the purified samples A, B, and C of the atomic weight work already referred to, some of which had not been used, and some of which had

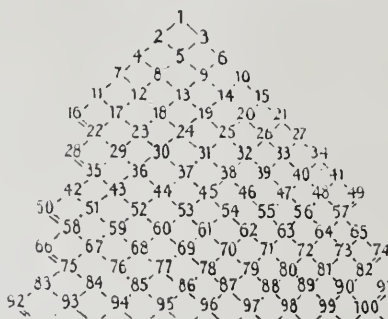
No attempt was made to purify further at this stage, because the unavoidable introduction of much silica during the fractionation (as well as possible accidental contamination) made necessary the thorough purification to which the samples were subjected just before the final tests.

Fractional Crystallisation.

The method of crystallising the nitrate by cooling the boiling nearly saturated aqueous solution was adopted after preliminary experiments on the chlorate and perchlorate of lead had indicated the superiority of the nitrate to these more soluble salts for the work in hand.

This superiority consists in the well-known habit of the nitrate of forming compact, large prisms on crystallisation from water solution, which can be very completely freed from mother-liquor merely by drainage, as well as in its slight tendency to supersaturation, and the consequent rapidity with which crystal-liquid equilibrium is attained.

The whole of the nitrate was then dissolved in distilled water and evaporated until a crust began to form. This was called Fraction 1. After cooling to room temperature the mother-liquor was poured off and formed Fraction 2. To the crystals from Fraction 1 was added sufficient water to dissolve them, and the solution was called Fraction 3.



953 954 955 956 957 958 959 960 961 962 963 964 965 966 967 968 969 970
971 972 973 974 975 976 977 978 979 980 981 982 983 984 985 986 987 988
989 990 991 992 993 994 995 996 997 998 999 1000 1001 1002 1003 1004 1005 1006

SCHEME OF FRACTIONAL CRYSTALLISATIONS.

The upper part of the diagram depicts the arrangement of the first 100 crystallisations. It contained 16 tiers of fractions. Fifty-six tiers of fractions, including 853 crystallisations, are omitted from lack of space. The last three tiers are given at the bottom of the diagram.

been recovered from the completed analyses. The samples of metallic lead which had been used in spectrographic tests and density determinations were also added, as well as all the mother-liquors remaining from the preparation of the purified samples. Much of this material was already in the form of nitrate, some in the form of chloride, and some was metallic. The chlorides were converted into nitrates by repeated evaporation with pure nitric acid, and the metal was dissolved in the same acid. All the nitrates were then combined, dissolved in the least possible quantity of boiling water, and precipitated by the addition of large quantities of pure concentrated nitric acid and cooling in an ice bath. The crystals were separated from the mother-liquor with a porcelain funnel, washed with concentrated nitric acid, and the washings and mother-liquor united. The strongly acid mother-liquors were evaporated to fuming with sulphuric acid, and the sulphates almost completely precipitated by dilution. The sulphates were converted to carbonates by boiling with sodium carbonate, washed nearly free from sodium, and dissolved in nitric acid. The small amount of nitrates thus obtained was evaporated to dryness and added to the bulk of the nitrates.

Fractions 2 and 3 were evaporated to saturation and cooled as Fraction 1 had been, the liquor from 2 forming Fraction 4. Fraction 5 was made by adding the liquor from 3 to the crystals from 2, and water was added to the crystals from 2 to form Fraction 6. This process was continued as shown in the diagram until, as occurred first with Fraction 16, one of the end fractions became too small to work with conveniently, and was consequently added entire to the mother-liquor from Fraction 17 to form Fraction 22. This expedient was resorted to wherever the end fractions became inconveniently small. In all, 75 courses or tiers of fractions were obtained, most of the last of which contained 18 fractions to a tier. The number of the last fraction was 1006.

The crystallisation was carried out entirely in porcelain, at first in large evaporating dishes, then, as the fractions became smaller, in casseroles covered with watch glasses. The hot casseroles were usually set in evaporating dishes full of cold water, which was frequently changed to hasten cooling. The fractionation was stopped after about 2000 repetitions because, since an accuracy of 2 per cent was hoped for in the final tests, 2000 fractionations would show

whether a difference in solubility amounting to one part in 50,000 for a single crystallisation existed or not. In other words, if the end fractions tested at this point showed no difference in the relative concentrations of their components, within the expected error of measurement of 2 per cent we should have proof that no complete separation could be attained by this method in less than fifty thousand fractionations.

Through the courtesy of Prof. Gregory P. Baxter, the facilities of the T. Jefferson Coolidge Memorial Laboratory were extended to one of us during the summer of 1916, when this part of the work was carried out. Thanks are due to Prof. Baxter, not only for this kindness, but also for many helpful suggestions which his experience with rare-earth separations made doubly valuable.

Repeatedly the advantage of centrifugal separation of mother-liquor from crystals has been demonstrated in cases of ordinary crystallisation where the crystals and mother-liquor are very different in composition. It is possible to show, mathematically, however, that where there is no such great difference the advantage of centrifugal draining is very much less, and in the present case it was found by this calculation that the gain in effectiveness of separation was less than the disadvantage caused by the increased time necessary for the centrifugal treatment of the thousand precipitates. Making the reasonable assumption that the difference in solubility in this case is probably not greater than 2×10^{-5} the relative advantage of centrifugal over gravitational drainage is seen to be certainly not greater than 1.5 : 1, so that it would be hopeless to try to increase the rapidity of separation by this means. Even under the best conditions with multiple-basket power centrifugals which could be stopped almost instantly, the time required would certainly be more than half again as much as for mere gravitational drainage. Therefore, in the present case, centrifugal draining was not adopted. Baxter, in his crystallisations of praseodymium and neodymium compounds, had come to the same conclusion from practical experience. A note discussing this matter mathematically will soon be published by one of us.

(To be continued).

AN UNIQUE BRITISH INVENTION.

A RUBBER MANUFACTURING SECRET CREATES A
NEW INDUSTRY.

A NATURAL sponge is a fascinating object. It interests the infant splashing in a bath; its wonderful design, composition, and qualities astonish the average user; scientific men have written learned treatises on its origin, sustenance, reproduction, and distribution. Scarcely less attractive is the artificial sponge—the red rubber oval that blushes in chemists' windows. In the artificial article man has imitated Nature closely and cleverly, though, up to now, never completely; and it has been left to an Englishman to discover the manufacturing secret of a product that equals the natural sponge in several respects, and excels it in many others.

Probably not one person in a thousand knows that hitherto rubber sponges have been made almost exclusively in Russia. Materials and their proportions, the method of manufacture and factory processes were carefully hidden, defying the prolonged efforts of American, German, and other investigators. For fifteen years the Russians held a monopoly, and every rubber sponge used in British bathrooms and businesses was imported from Kerensky's country—and only during the last five years have they had to face competition, and that from America. Now there is no need to go abroad. An English inventor, Mr. G. W. Leeson, after laborious experiment, has produced an artificial sponge superior to any forerunner, inasmuch as it is

lighter, cleaner, softer, and odourless, full of elasticity, more durable and more absorbent.

Like many another discovery, the original rubber sponge was due more or less to an accident. In making certain rubber goods a "fault" was developed, its cause was traced, and out of this "fault or flaw" the artificial sponge emerged. Subsequently it was improved by the Russians and Americans; it has now been perfected by Mr. Leeson, whose production is not merely a by-product, but an invention pursued for itself.

The texture is finer, the air cells are more numerous, and the touch is like that of velvet. Even on the tenderest skin, with or without soap, there is not the slightest trace of roughness. In colour the Sorbo, as the sponge is called, resembles the hue of the natural sponge and retains it; for, while the latter becomes foul and slimy, the Sorbo retains its freshness, this after a service four or five times longer than the ordinary article.

Mr. Leeson is full of confidence as to the commercial future of his invention. "The demand for sponges is practically unlimited," he said, in the course of a ten minutes' chat. "Hospitals are large buyers at any time; just now the demand is a hundredfold greater. My sponge is absolutely sanitary. The worst wound may be dressed with it, and no disinfectant or antiseptic lotion has any ill effect on it."

"There's another thing I would like to say," he continued. "Sponges are not used so much for household purposes as they might and ought to be. No careful housewife should be content to clean or polish with any old rag. Carpets, for example, are better for being sponge-cleaned; so are fine furniture, china, porcelain, and kindred articles. Sorbo does not leave the tiniest scratch on the finest art treasure."

"Cleaning furniture! Might as well add the motor car," I suggested.

"Certainly," Mr. Leeson replied; "Sorbo sponge is just the thing for brightening up paint and varnish, and it will last longer at the job than any other."

"How are you going to convince people of this Sorbo superiority?"

"Well, we have under consideration various schemes. We have a big exhibition at Whiteley's in Westbourne Grove, and doubtless we shall do something with others in London and with kindred concerns in the provinces."

So, soon we shall hear more about a wonderful invention which is likely to penetrate into every household, from the humblest to the highest, into civil and military institutions, everywhere performing functions that contribute to the comfort and health of the whole human family.

THE MYSTERY OF THE TRANSPARENT RAT.

CHEMICAL NEWS SHOWN TRANSPARENT MICE,
FROGS, FISH, AND ANATOMICAL SPECIMENS.

(From a Representative of the CHEMICAL NEWS).

THE story of the transparent rat at the South Kensington Museum, reported in the CHEMICAL NEWS of June 1st (cxv., 260), has created considerable interest, and to obtain more light on the subject, a representative visited the museum the other day, and asked Dr. S. F. Harmer, F.R.S., if he would be so good as to enter a little in detail in explanation of the mystery. Dr. Harmer was kind enough to do so, and at the same time to produce half-a-dozen such specimens—all transparent—rat, mouse, frog, fish, and so on.

Dr. Harmer has asked the Board of Trade to grant him a licence to employ a German patent, 8621 of 1909, for producing such specimens, and the principle, as Dr. Harmer described it, by which the transparency is secured is the immersion of the specimen (after due preparation)

in a liquid which has the same refractive index as the tissue which it is desired to examine, or else, more generally, the same refractive index as the mean of the indices of the various tissues of which the body is composed.

The principle may be illustrated by a glass tube. The tube from its surface ordinarily reflects lights and objects. Light rays are throwd upon it from various quarters. Placed in water, however, its aspect becomes much more transparent. Placed in a liquid having the same index of refraction as the material of the glass, the tube is hardly visible at all.

The body of an animal contains various cavities, the cavities occupied by organs. A ray of light passing through would be deflected at the surface of each new medium both where it passed in and where it passed out. This fact, together with the amount of dark colouring pigment in the body, has its bearing on the opacity of the object. Remove the dark pigment and place the body in a medium having the same index of refraction as its own, and the undoubted optical result is at once a considerable advance in the direction of transparency.

A good example, by the way, of the opaque result of bending rays of light out of the straight is "ground glass," in which the surface is so broken up that the separate rods of light do not pass through in a direct line at all. The glass, therefore, is not "transparent."

The effect of colour pigment in a body was strikingly seen in the transparent rat, the first of the specimens Dr. Harmer placed on the table. The rat, with legs extended, hangs immersed in an oblong glass vessel. He is singularly transparent. His skeleton is his most salient feature, but that, too, is transparent in a sense. The bony articulations of his tail at first take one's attention, because of their detached regularity and the thin line on either side of the chain which marks the limit of his skin. His body, of course, has not the same water-like absence of colour of the fluid. It has a yellowish look, as of something gelatinous, and in the thighs is a certain cloudy bluish opalescence. But the body, through the film which indicates it, is clearly transparent, and every bone is seen "in the round," with the organs reposing in the interior, as surely as when one opens a turkey on the kitchen table.

The ears the spectator must specially look for, or he would miss them altogether. They are more intangible than wetted goldbeater's skin, and hang over with the same clinging folds.

It is the liver, however, which shows what colour means to this process. It is simply a large, inky, irregular mass, packed with black pigment, the one blot in the transparent scheme, and it declares in the most uncompromising fashion that indices of refraction have nothing to say to the blank opacity of dense colour.

This fact, then, is duly taken into account in the preparation of the body. All dark pigment, as far as possible, is removed, and the skin is bleached. The rat does not go into the solution wearing his fur overcoat. He has been reduced to the unesthetic nakedness of the rabbit on the poulterer's slab.

He goes through more than one sea of solution before he draws up in the anchorage of the object glass. First, the water that the tissues naturally contain must be removed. All organic bodies carry a considerable proportion of water—the human cardiac muscle, for instance, 80 per cent.

One has to employ a series of fluids which mix, with water on the one hand and with oil on the other. The rat goes first into alcohol, weak. This is gradually strengthened till, all water expelled, the rat is in pure ethyl alcohol. A fluid must then be introduced which mixes equally with alcohol and with oils, and the rat comes eventually into pure benzol, in order to get rid of the alcohol. It is, of course, necessary to keep him in a state of being permeated by some liquid through all the stages, or he would collapse and lose his natural shape.

An air pump is brought into play, and he passes through a vacuum into the liquid with the same index of refraction

as his own; and this henceforth (when the bottle has been sealed) becomes his home.

Something like the same process is employed in mounting slides for the microscope. If it is desired to mount a flea, the flea, being full of water, must be treated scientifically, and the water has to be got rid of before you can transfer him to the Canada balsam, the substance usually employed for mounting microscopic slides.

Equally, if one cut off a person's hand, the anatomist would treat it in the same way as the rat, in order to bring it to a state of eventual transparency.

An example of a liquid, the index of refraction of which corresponds to most of the animal tissues, is a mixture of three parts of salicylic methyl ester and one part of benzylbenzoate.

Various specifications of liquids with different indices of refraction are set out in a German booklet Dr. Harmer possesses, written by Dr. Spalteholz, the second edition of which was published in Leipzig in 1914, the year the war broke out. This is the "Über das Durchsichtigmachen von menschlichen und tierischen Präparaten und seine theoretischen Bedingungen."

The professor gives the following—

	Index of refraction.	Specific gravity
Wintergrünol (or oil of wintergreen) ..	1.538	1.188
Safrol	1.542	1.102
Benzyl-benzoate	1.570	1.121
Isosafrol	1.577	1.115

If the body which is to be made transparent has an index of refraction of, say, 1.560, the appropriate solution would probably be a mixture of safrol and benzylbenzoate, and experiment would determine the proportions.

Beginning with the lower, and adding a fluid of higher refractive index, he would see the object becoming progressively more and more transparent, and thus the experimenter would "focus" it.

"In some cases," Dr. Harmer quoted, "liquids may be chosen which, by virtue of their index of refraction, cause certain parts or groups of the body to disappear, so to speak, and thereby bring other parts more prominently into view."

Thus it is possible, if the anatomist is concerned only with the muscles, to arrange a solution with the same index of refraction as the muscles, and to ignore the different index of refraction of the bones, by means of which, in the result, the bones would be optically obscured in the specimen.

On the same principle, on the other hand, the bones can be brought principally into view. Professor Spalteholz gives several solutions for revealing human decalcified bone; for instance—

5 parts of oil of wintergreen	and 3 benzyl-benzoate, or
3 " " "	and 1 isosafrol, or
3 " safrol	and 1 of benzyl-benzoate.

Dr. Harmer, going through his curious objects, produced an intestine in a case, the tissue almost invisible in the solution. The blood-vessels, by reason of an injected red matter, stood out like a network of coral. The circular tube of the colon might have been gossamer fabric of skeleton-leaf. One could see a cherry-stone traverse its entire length.

Dr. Harmer has also a transparent mouse and a transparent fish, the latter showing with fine definition the air-bladder and the rays of the fins along their entire length, so clear that they may be counted.

A frog, just coming to the surface, is another interesting "macragraph," and a larger case contains a tiny hand, arm, and shoulder-blade, the fingers extended, the bones of the forearm and clavicle shown separate and disjointed, and the muscles and arteries daintily outlined—the whole making a very beautiful and successful specimen.

WELFARE WORK IN FACTORIES.*

By B. SEEBOHM ROWNTREE.

IT is a time of national stocktaking, and the Government is trying to find out its actual resources in the way of potatoes, flour, sugar. I want to speak of an asset which cannot be precisely weighed or measured, although it gives their value to all our other assets. I mean the vitality of the nation as a whole.

At any given moment, on the credit side of a nation's life, there is so much staying power, so much energy, so much physical and mental fitness—in a word, so much health, with all the conditions which make for health.

On the debit side are all the conditions and forces and maladies that sap and prematurely waste health.

To-day, we have had to abstract from the sum of human force, strength, and skill that should be pledged to the nation's service, whether on the battlefield or in the factory or on the land, the long roll of the "physically unfit for any useful occupation." But they are not a mere deduction from the credit side. Speaking roughly, each of them must be placed on the debit side. If we consider the statistics of infantile mortality—so much heavier proportionately in some parts of the town than others, and among the poorer classes—we see that there is a huge leakage somewhere. But death is only an extreme form of that leakage which is always going on.

Now, welfare work is very largely the attempt of employers of labour, in their own sphere, to increase the nation's assets of health and to diminish or cut off all leakage and breakage, all squandering of vitality.

It should aim, in the first place, at establishing a really satisfactory level of wages. I mean a level which shall not only cover the bare demands of physical efficiency, but provide a substantial margin for such expenditure as will increase health by the potent method of increasing happiness. Gardens, hobbies, holidays, books and pictures, even companionship, are largely bound up with the existence of the margin.

But high wages which make for health may be associated with working hours that tax it far too heavily. A man starved of rest is in no better position than a man starved of food. Sooner or later there comes a breaking point, when he is bankrupt of health. It is one of the aims of the welfare movement to correlate effort with capacity. A human being is not a candle to be burned at both ends, or even one end, but a lamp, to be kept from breakage and kept replenished with wick and oil.

Next we come to hygienic conditions. Adequate light, pure air, a good canteen, where nourishing food may be obtained and eaten in comfort, medical attendance, hospital cupboard, rest rooms for cases of illness and exhaustion, adequate sanitary accommodation, cloakrooms where wet things can be taken off and dried—all these come under the supervision of the welfare worker, and all directly benefit the health of the employee.

But it is also benefited by the organisation of recreative facilities—cricket, tennis, the provision of gymnasia, swimming baths, &c., schemes of allotments on a self-supporting basis, &c., and by the facilities for sending workers, when necessary, to convalescent homes.

The provision of comfortable means of transit to and from work, and of suitable housing accommodation for young employees living away from home, are all relevant to welfare work. The establishment of sick clubs, pension schemes, &c., all tend to diminish anxiety and thus to promote the health of the workers.

I come last to an indirect but important relation between welfare work and the public health. The welfare movement aims at creating a spirit of cordial co-operation and an atmosphere of goodwill and mutual understanding which shall pervade the whole factory, and affect each in-

dividual. The discontented worker will never be really healthy. Even a trivial grievance that is left unredressed soon begins to rankle and cause blood-poisoning in the body industrial, and all such maladies of mind or soul react on physical health. Contentment, on the other hand, is a very great physician. His fees are high, but we cannot afford to dispense with him.

INCREASED FOOD PRODUCTION.

IMPORTANT RECOMMENDATIONS.

RECOMMENDATIONS which probably represent the expert opinion of the majority of United Kingdom agriculturists are set forth in resolutions adopted by the Executive Committee of the Agricultural Section of the British Empire Producers' Organisation. The members of the section are connected with the most influential and representative agricultural associations in the country, and the main interest of the recommendations lies in the warning conveyed that our food supply will not necessarily increase in proportion to the mere acreage of grass land broken up under official instructions. Briefly summarised, the resolutions claim that the ploughing of pasture land should not go far in advance of visible means of proper cultivation in regard to labour, seed, machinery, fertilisers, horses, and so forth; that War Agricultural Committees should be instructed to require a certain total quantity of cereals from each county; that in such case better results may be obtained from intensive cultivation of existing arable land than from breakage of less promising pasture; and that some guarantee of compensation for loss would act as an incentive to farmers who naturally hesitate to attack land of doubtful quality as a personal speculation. A copy of the full resolutions may be obtained from the General Secretary at Kingsway House.

Resolutions.

1. The Committee, whilst desirous of doing everything in their power to assist the efforts of the Government to bring a large additional area of suitable land under arable cultivation, view with grave concern the instructions now being issued in counties to break up indiscriminately a specified acreage until definite provision has been made for supply of labour, seed, horses, machinery, and capital adequate to maintain the whole area of arable land in a proper state of cultivation.
They strongly recommend the revision of the task imposed on the War Agricultural Committees, so that the approximate total quantity of cereals required from each county shall be stated and it be left to those bodies to take such steps as in their opinion are best calculated to produce the desired result, having due regard to the preservation of ample supplies of milk and wool.
2. The Committee are of opinion that, provided the milk supply is fully safeguarded, a greater concentration in the present area of arable land, and the substitution of cereals for root and other crops would much reduce the area of grass land that would otherwise have to be broken up. This can only be done effectively if a sufficient supply of fertilisers is guaranteed.
3. The Committee feel that a definite pronouncement by the Government that owners and occupiers of land will be compensated for any loss they may suffer in carrying out the recommendations of the Board or the County War Agricultural Committees would greatly assist in increasing the arable area.
4. That the above Resolutions be forwarded to the Prime Minister, President of the Board of Agriculture, Lord Selborne's Agricultural Reconstruction Committee, agricultural bodies, and the Press.

* Abstract of Lecture delivered at the Royal Institute of Public Health, June 6, 1917.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, May 24, 1917.

Sir J. J. THOMSON, O.M., President, in the Chair.

PAPERS were read as follows:—

"Influence of Vibrations upon the Form of certain Sponge-spicules." By Prof. A. DENDY, F.R.S., and Prof. J. W. NICHOLSON, F.R.S.

It has been suggested recently by one of us that the positions of the whorls which appear on certain siliceous spicules in the genus *Latrunculia* may be determined by vibrations to which the spicule is subjected at a certain stage of its development, corresponding, in fact, to the nodal points of a vibrating rod. The object of the present communication is to describe a similar case in a closely allied, but hitherto undescribed, genus, and to subject it to mathematical analysis with a view to testing this vibratory theory.

The problem was to determine the degree of coincidence between the actual positions of the whorls on the spicule and the positions which would be occupied by the nodes in a vibrating free-free rod of shape similar to that of the shaft of the spicule at the moment when the nodes are beginning to develop (*i.e.*, at the critical stage). In order to solve the problem, it was necessary, in the first place, to determine the theoretical positions of the nodes in certain cases intermediate between the uniform rod and the rod in the form of a double cone. From the exact solutions of suitably selected mathematical cases, an interpolation formula was found, from which the positions in any intermediate case, to which an individual spicule might belong, could be determined at once. The general problem is that of the nodes in a rod composed of two equal portions, each formed by the rotation of the curve $y \propto x^n$ between $x=0$ and $x=l$ about its axis, and the positions of the nodes are expressed as functions of the index n by the interpolation formula. All the spicules examined correspond very closely with this law of shape for values of n between $\frac{2}{3}$ and 1.

Details of ten cases at or near the critical stage are given in the paper, and the conclusion is arrived at that the positions of the whorls, although subject to slight individual variations due to various disturbing factors, agree so accurately with the theoretical positions of the nodes as to leave little doubt as to the influence of transverse vibrations in determining them. An efficient cause of such vibrations may be found in the water currents which circulate with considerable force through the canal system of the sponge.

"The Lateral Vibrations of Bars of Variable Section." By Prof. J. W. NICHOLSON, F.R.S.

The paper contains a discussion of the lateral vibrations of a bar composed of two equal halves and free at each end. Each half consists of a portion of the solid generated by the revolution of the curve $y = Ax^n$ about its axis, and the fundamental frequencies and positions of the corresponding nodes are investigated for various values of n between 0 and 1.

The investigation proceeds according to a general method of determining the period equation as a series of ascending powers of a variable whose general term can be found from a differential equation of the sixth order. The special values of n for which computations are made were selected in accordance with the needs of another paper on the vibrations of sponge-spicules communicated to the Society by Prof. Dendy and the writer.

The dependence of the frequency and nodal distance on the index n is finally expressed by interpolation formulae which can give an accuracy of about 1 part in 100 within the range $n = 0$ to $n = 1$.

PHYSICAL SOCIETY.

Ordinary Meeting, May 25, 1917.

W. R. COOPER, M.A., Vice-President, in the Chair.

A PAPER, entitled "*An Investigation of Radium Luminous Compound*," by C. C. PATERSON, J. W. T. WALSH, and W. F. HIGGINS, was read by Mr. PATERSON.

The paper contains the results of measurements made on various samples of radium luminous compound during the last two years. Determinations of the brightness of the compound in powder form and when made up into paint, and also after the application of the paint to instrument dials, were carried out; and curves are given showing the rates of decay of luminosity. The radium contents of the compounds were determined by comparison of their γ -ray activities with that of a preparation of pure radium bromide, which is periodically compared with the British radium standard. The various precautions which have to be observed and the corrections which have to be applied in making the various determinations are explained, and the considerations which should govern the proportion of radium employed for practical purposes are discussed.

DISCUSSION.

Mr. F. H. GLEW—The difference between some of Marsden's result and those of Dewar and Crookes had been attributed to some difference in the zinc sulphide employed; he could state that the sulphide supplied to the National Physical Laboratory was of different origin from either of these. Before the war we were almost entirely dependent on foreign sources for the supply of these materials, but we are now quite self-supporting. In Marsden's work the inside of the tube was completely coated with sulphide, so that the effects were observed by light transmitted through the material. It was better to paint only one half of the tube so that the inner surface, which was exposed to the bombardment, could be directly observed. In the photometer measurements, was there any advantage in placing the coloured filter between the light and the reflecting surface? He preferred to have it in the eye-piece. Earlier records of the coloration due to absorption would be of value. In testing sulphide for γ -ray activity he placed it in contact with the ionisation chamber. Less material was then required for the test, which was an advantage. The authors state only the diameters of the tubes employed; but he had found that there were differences in the results obtained with tubes horizontal or vertical. The length of the tube, therefore appeared to be an important factor. Further, the results given by a small quantity of sulphide in a large tube would be too high; for the space above the sulphide is filled with the emanation gas, and the γ radiation from it is not subject to the absorption of the sulphide, as is the radiation from the latter itself. The discrepancy between the observed and calculated values of the absorption was probably important. Was this due to some selective action, the sulphide transforming the γ radiation into radiation of some other type? It was singular that specimens prepared by the dry and wet methods should be so similar in their properties after only four days; for in the dry method the emanation and all its products are retained.

Dr. MAKOWER stated that by using an electroscope of small capacity good γ -ray measurements could be obtained with much less than 1 mgrm. of radium.

Dr. H. S. ALLEN asked if the zinc sulphide employed was wholly crystalline or partially amorphous. An investigation of its physical condition would be useful.

Prof. CLINTON said that the difficulties of these measurements were very great and the authors were to be congratulated on having overcome them so effectively.

Mr. J. S. DOW said the figures for the absolute bright-

ness were what he would have expected. He was doubtful of the possibility of expressing the brightness accurately; consistent results could be obtained, but they did not represent exactly what the eye saw. For instance, zinc sulphide and cadmium sulphide may be equally bright a few inches away, but the former will look much brighter at a distance. The information as to the correct proportion of radium to employ was important. What was the brightness physiologically necessary for these purposes? He thought that less brightness than was customary might be advantageous, as he sometimes experienced an appreciable glare from the markings, which detracted from their legibility. The selection of a proper coloured glass was important for these measurements. Had the authors noticed any change of colour as the compound got older? He thought it got greener as it aged. The initial rise in the luminosity curves for the weaker material seemed greater than could be explained by the lower rate of decay.

Dr. LEVY said he had found the luminosity of different samples of zinc sulphide to vary perceptibly in tint when stimulated by daylight, but had not noticed this with α -ray stimulation. In his experience, if a sample of sulphide gave good results when stimulated by daylight, it would also be good when stimulated by radium. The reverse did not hold, however, as a specimen might be poor with daylight but good with radium excitation.

Mr. T. SMITH thought the coloured filter used in the photometric measurements should have been placed as near the lamp as possible, since such a filter acts, to a certain extent, as a self-luminous source. If the tube containing the compound was not much wider than the aperture in the screen, a considerable loss of light would occur, near the edges of the aperture, due to oblique internal reflection at the walls of the tube. For accurate work it was important to have a uniformly illuminated field, and he suggested the desirability of employing tubes with a flat side. Where the tubes were too small to fill the aperture satisfactorily, an optical system could be used to give an enlarged image of the tube and so avoid refractions at large angles. The absorption of the system could be found experimentally with a larger tube.

Dr. A. RUSSELL laid stress on the practical importance of the paper. He had at times been asked by manufacturers to measure the visibility of watch faces in the dark. The problem was so difficult that hitherto he had done nothing. The present paper suggested the required practical tests, and a first draft of a specification for securing a standard material could now be written. Progress would be delayed if they waited till all the associated physical and physiological problems were cleared up.

Dr. S. RUSS (in a communication which was read by the Secretary) said the decay curves differed appreciably from those of Marsden for Willemite under intense α -ray bombardment. Did the theory held by the authors as to the mechanism of the action differ from that advanced by Prof. Rutherford to explain Marsden's results? Had the authors any measurements of the rate of decay of efficiency of fluorescent screens under the action of X rays?

Mr. WALSH, in reply, said that if the coloured filter were employed in front of the eye, as suggested by Mr. Glew, its coefficient of transmission for the light emitted by the compound would require to be determined and introduced in the results as well as the coefficient for white light. This would add to the uncertainties of the determinations. To detect change of colour with age would have been difficult in their experiments because of the continuous decrease in luminosity. They had detected differences in colour in samples sent by different makers; but were unaware whether these were from the same source, or made in the same way. They had no data on the relation between daylight and radium excitation, and Dr. Levy's remarks were of great interest. The order of accuracy (about one per cent) was not found to be appreciably affected by altering the position of the coloured

screen. The diameter of the smallest tubes usually employed was not less than about twice the apparent width of the aperture. It was not convenient to use a smaller aperture, and they had to do their best with the tubes in which the material was sent.

Mr. HIGGINS, replying to Dr. Makower, said that they had to employ the radium standards which were available, and these were not suitable for use with a small capacity electroscope. In reply to Mr. Glew, the tube should not be close to the electroscope. If it was 30 to 40 cm. off, the orientation of the tube was of little importance, and small corrections could be applied. The errors introduced by having it too close were similar in character to those produced if an extended source of light is used too near a photometer head. They suspected selective action to be at the root of the discrepancy in the absorptions, but could not definitely say. To investigate the physical properties of the sulphide would be a very long task, and they had not attempted it in the present research.

A paper, entitled "*The Resistance to the Motion of a Lamina, Cylinder, or Sphere in a Rarefied Gas*," was read by Mr. F. J. W. WHIPPLE. (Abstract).

The investigation is carried out on the assumptions that the free-paths of the particles of the gas are long compared with the dimensions of the moving body, and that the motion, relative to the body, of the particles which rebound from it depends only on its temperature. It is shown that if v , w be the components of velocity perpendicular to the surface of a lamina and parallel thereto, the corresponding components of the resistance are—

$$(+ \pi) \sqrt{\frac{3}{2\pi}} \frac{v}{V} p \text{ and } 2 \sqrt{\frac{3}{2\pi}} \frac{w}{V} p,$$

where V is the standard (root-mean-square) speed of the gas-particles and p is the gas-pressure.

The resistance to the motion of a cylinder or a sphere is found to differ very slightly from the resistance to a lamina occupying the central section. The formulæ are applicable to the problem of the damping of the oscillations of a system suspended in a rarefied gas.

DISCUSSION.

Mr. G. D. WEST called attention to the fact that the author's value for the ratio of the normal to the tangential resistance of a lamina, was in good agreement with that previously obtained by Knudsen. This experimenter had also deduced a formula for the resistance of a sphere moving in a rarefied gas, and it would be interesting to see how this result compared with the author's. In connection with the damping of vibratory motion, a large amount of careful work had been done by Hogg.

Mr. D. OWEN was not sure that Knudsen had succeeded in proving the assumption as to the manner in which the gas molecules recoiled from the surface. As the difference involved was somewhat large, he would like to see an expression added for the case of elastic spheres rebounding off a perfectly plane surface.

The formula holds only for values of λ large in comparison with the dimensions of the vessel. If the pressure is 1μ , $\lambda = 19$ cm., and if 10μ it is 2 cm. Would this be called large in comparison with dimensions of 10 cm.? Exact measurements of pressure and damping would be interesting in view of the uncertainty of the exact constant.

A communication from Dr. P. E. SHAW has been received. It will appear in the *Proceedings*.

A paper, entitled "*The Effect of Stretching on the Thermal Conductivity of Wires*," by Prof. C. H. LEES, F.R.S., was taken as read.

Mr. W. R. COOPER, M.A., Vice-President, has presented a copy of his book on "Primary Batteries" to the Society's Library.

SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS.

Ordinary Meeting, June 6, 1917.

MR. GEORGE EMBREY, President, in the Chair.

CAPT. N. M. COMBER, A.R.C.S. (Lond.), was elected a Member of the Society.

Certificates were read for the second time in favour of Messrs. Charles V. Bacon, and Kapilram Hardevram Vakil, B.A. (Bombay), B.Sc.Tech. (Manch.).

The following papers were read:—

"Some Experiences in the Use of Copper Sulphate in the Destruction of *Algae*." By GEORGE EMBREY, F.I.C.

Water in certain reservoirs, until the introduction of copper sulphate, became in summer distinctly green, and had an aromatic smell. This was first ascribed to a species of *Chara*, but later to the diatom *Asterionella*, which has at times been found in conjunction with *Tabellaria*. The chemical actions appeared to be that the copper was first changed to copper carbonate, then to hydrate, and finally to the cuprous and cupric oxides, which latter probably formed the real *algæ*sides.

"A Combined Reichert-Polenske and Modified Shrewsbury-Knapp Process." By G. D. ELSDON, B.Sc., F.I.C.

The author has combined the modification of the Shrewsbury-Knapp process recently suggested (Elsdon and Bagshaw, *Analyst*, 1917, xlii., 72) with the Reichert-Polenske process; the new process results in a great saving of time, it being possible to obtain results in from two to two and a-half hours. Figures are given for mixtures of coconut oil with butter and with margarine, and also for pure butters. Certain criticisms offered on the previous papers are replied to.

"The Differentiation between Coconut and Palm Kernel Oils in Mixtures." By G. D. ELSDON, B.Sc., F.I.C.

The author suggests a method for the estimation of coconut and palm kernel oils in the presence of each other by taking into account both the Polenske and the Shrewsbury-Knapp value. The Polenske value of these oils is very different (17 and 11 respectively), whilst the Shrewsbury-Knapp value is practically identical. Certain objections are considered, and the composition of twelve samples of commercial margarine is given, in five of which palm kernel oil is shown to be present.

"Note on Orange Pip Oil." By DOROTHY G. HEWER, B.Sc.

The analytical figures are given for a sample of bitter orange pip oil, extracted by means of petroleum ether from a commercial sample of the pips. The only published figures for this oil seem to be those of R. Meyer (*Chem. Zeit.*, 1903, 958) given by Lewkowitsch, and these are no altogether confirmed. The commercial utilisation of the oil is discussed.

"Rapid Estimation of the Strength of Sulphuric Acid." By H. DROOP RICHMOND, F.I.C., and J. E. MERREY-WETHER.

The heat evolved on dilution is utilised as an analytical method for the determination of the strength of sulphuric acid; a convenient apparatus is described, and a formula connecting rise of temperature and strength given.

"Estimation of Theobromine." By NORAH F. ELLIOT, B.Sc., and G. BREWER.

In Kunze's method and Monthulé's modification the estimation of theobromine depends on a silver estimation in the silver theobromine compound. The results are vitiated by the presence of any substance giving an insoluble silver salt, or what is more usual, reducing silver, and the results are too high. Accurate quantitative results can be obtained by nitrogen estimations.

NOTICES OF BOOKS.

Gas Chemists' Handbook. Edited by A. F. KUNBERGER. New York City: The American Gas Institute. Pp. 354.

FOR the publication of this report the Committee on Chemical Tests has carried out a thorough revision of the last edition of the "Gas Chemists' Handbook," published in 1914. The chief aim of the Committee since that date has been to standardise methods of testing and sampling, and the processes which have been found most reliable are very carefully and fully described in this edition. The directions for the practical work are worded accurately and clearly, and methods of calculating the results are described without any discussion of the deductions to be made from them. Although the book is designed chiefly for the use of trained chemists, those who had but very little experience would find themselves well able to carry out the experimental work described in it, and if they exercised due care could hardly fail to get satisfactory results. The methods described include the testing and sampling of raw materials, the products of gas manufacture, including tar and derivatives of tar, and also some constructive materials and lubricating oils.

CORRESPONDENCE.

RE NEW ELEMENT.

To the Editor of the Chemical News.

SIR,—I notice in the CHEMICAL NEWS for April 20 (cxv., 182) an account of an element which comes down in the iron group, by W. Bramley, which appears to have some peculiar properties. I have little hesitation in stating that the element in question is Europium, which up to the present time has only been found in extremely small quantities. I find that the spectrum is the best means of detecting the element with certainty. For purposes of analysis the arc spectrum is the best.

The lines most suited for the detection of the element are as follows:—

3688.57	3725.10
3819.80	3907.28
3930.66	3972.16
4129.90	4205.20
4435.75	4522.76
4594.27	4627.47
4662.10	6645.44

—I am, &c.,

S. C. F. LISTER.

Warninglid Grange,
Hayward's Heath, Sussex.

MISCELLANEOUS.

Society of Glass Technology.—A joint meeting of the Society of Glass Technology with the Faraday Society will be held at the Applied Science Department, The University, St. George's Square, Sheffield, on Wednesday, June 20, at 3.30 p.m., when a discussion will take place on "The Choice of Refractory Materials for use in the Glass Industry." The discussion will be opened by Prof. W. G. Fearnside, M.A., with a paper on "Supplies of Refractory Materials for use in the Glass Industry." The following papers will also be communicated:—"Stone and Fireclay Blocks for Glass Tank Furnaces," by J. H. Davidson, M.Sc., and "The Drying of Glass Pots," by J. W. Mellor, D.Sc. Prof. P. G. H. Boswell, D.Sc., and Mr. Cosmo Johns, M.I.M.E., are also expected to contribute to the discussion. Communications on the subject are invited from members.

NOTES AND QUERIES.

Manufacture of Glycerin.—A correspondent asks for particulars of the best English book on the commercial manufacture of glycerin.

THE CHEMICAL NEWS

Vol. CXV., No. 3004.

ON THE NATURAL OCCURRENCE IN CERTAIN FISH-LIVER OILS OF HIGH PERCENTAGES OF HYDROCARBONS.

By A. CHASTON CHAPMAN, F.I.C.

In September, 1915, a sample of oil was submitted to me with the request that I would examine it and state if it consisted of genuine cod-liver oil. The oil was of a pale yellow colour and had a pronounced odour of fish oil. In the course of its examination the following results were obtained:—

Sp. gr. (15°/15° C.)	0.8666°
Saponification value	22.5
Iodine value (Wij.)	358
Unsaponifiable matter	89.1 per cent.
Iodine value of unsaponifiable matter	376.2
Free fatty acid (as oleic acid)	0.42 per cent.
Bromine precipitate insoluble in ether	76.5 per cent.

I reported that it consisted of approximately 89 parts of some "unsaturated hydrocarbon oil" with approximately 11 parts of some fish oil. Had my examination been restricted to a determination of the specific gravity of the sample and to an estimation of the percentage of unsaponifiable matter present, it might have been reasonable to assume that the oil consisted of a mixture of mineral oil and fish oil; and I subsequently learned that, before it was submitted to me, this verdict had, in fact, been passed upon it. A consideration of the iodine value and the percentage of bromine precipitate insoluble in ether appeared, however, to exclude this explanation entirely.

The results, in fact, perplexed me very greatly, for I was not aware of any hydrocarbon or other unsaponifiable substance possessing the properties exhibited by the unsaponifiable matter present in this oil. It seemed very probable to me, therefore, that this was not an adulterated but an abnormal specimen of oil, and I decided for my own satisfaction to submit it to a systematic investigation.

A few weeks after the commencement of my investigation, I received a copy of a report which greatly stimulated my interest in the matter. The vendors of the oil in Lisbon repudiated the suggestion that it was adulterated, and submitted a sample to Dr. Hugo Mastbaum of that city, who obtained results similar to mine, and who expressed the same opinion.

As the vendors were still not satisfied, they submitted portions of the actual livers to Dr. Mastbaum, who again obtained very similar results with the expressed oil. Still not satisfied, the merchants in question invited Dr. Mastbaum to witness the opening of several fish and to take with him portions of the livers for examination. The two species of fish, which were opened in Dr. Mastbaum's presence, appear to be known in Portugal as "Barroso" and "Carocho" respectively. According to Mastbaum, these were about 1 metre in length, were quite fresh, and the livers were "smooth and oily, and when pricked with a knife, considerable quantities of oil immediately separated, the bulk of the liver substance being transformed in the course of a few hours into an oily liquid."

In a subsequent communication (*Chem. Zeit.*, 1915, xxxix., 139, 889) the following results were given by Mastbaum for these two samples of oil:—

	"Barroso,"	"Carocho,"
Sp. gr. (15°/15° C.)	0.8637°	0.8711°
Butyro-refractometer at 25° C.	102	93
Polarisation in 200 mm. tube	0.3	2.33
Solidification point	Still liquid at -7° C.	Becomes turbid at -7° C.
Saponification value	15.4	36.7
Free acids (calculated as oleic acid)	0.097 per cent.	0.165 per cent.

As I was unaware that Dr. Mastbaum had published this note, I wrote to him pointing out that I had completed the first part of an investigation of the oil, and asking him to give me any information he could in reference to its origin. He replied informing me that the oil in question was obtained from the two species of fish above referred to, and added the information that, according to a standard Portuguese dictionary, the scientific descriptions of the above fish are *Centrophorus granulosus* and *Scymnus lichia* respectively. He also informed me that these fish are caught in deep water off the Moroccan coast, and that they have only come into the Portuguese market since the employment of steam trawling in these fishing grounds. He suggests that it is owing to this fact that the existence of fish-liver oils containing so large a proportion of unsaponifiable matter has hitherto escaped observation.

Into the details of the investigation of this sample of oil it is unnecessary for me to enter, since a full account of the work has recently been published in the journal of the Chemical Society (*J. Chem. Soc.*, 1917, cxi., 56). It will suffice if I point out that the greater part of the oil was found to consist of an unsaturated hydrocarbon having the formula $C_{30}H_{50}$, and containing six ethenoid linkings, which, of course, accounts for the very high iodine value of the original oil.

Among the other compounds which I have prepared is a dodecabromide having the formula $C_{30}H_{50}Br_{12}$, which is insoluble in ether, and which is consequently obtained by the process usually adopted for the preparation of ether-insoluble brominated glycerides.

The hydrocarbon does not appear to be identical with any known hydrocarbon, and I have therefore proposed for it the name "spinacene," since both *Centrophorus granulosus* and *Scymnus lichia* belong to the *Spinacidae* or *Squalidae*—a family of the *Selachoides*, or sharks. It is optically inactive and does not solidify when cooled to -20° C. Its specific gravity at 15°/15° C. = 0.8611, and at 20°/20° C. = 0.8616.

The following are the results of determinations of its index of refraction at 20°:—

n_{Ha}	=	1.4932
n_D	=	1.4967
$n_{H\beta}$	=	1.5054
$n_{H\gamma}$	=	1.5130

At 150° C. its index of refraction for the D-line is 1.4987; its specific refraction calculated by the $\frac{n^2 - 1}{(n^2 + 2)d}$ expression, is 0.3394, and the molecular refraction 139.1.

Taking Conrady's average numbers for the atomic specific refractions, (D-line) $C_{30}H_{50}$ with six ethenoid linkings requires 137.7.

Employing the n^2 formula, the specific dispersive power of spinacene, $\gamma - \nu_a$ is 0.0114, and its molecular dispersion $(\gamma - \nu_a)M$, 4.67. Taking Eisenlohr's numbers for the atomic dispersions for the α - and the γ -hydrogen lines, the calculated number is 4.33. It will be seen, therefore, that the molecular dispersion, like the molecular refraction, is high. In this connection, it is worthy of note that both the molecular refraction and the molecular dispersion of the saturated hydrocarbon obtained from spinacene agree well with the calculated numbers.

TABLE A.

	Cod-liver oil.	Spinacene containing shark-liver oil.
One drop of a mixture of one volume of oil with one volume of carbon disulphide was introduced into concentrated sulphuric acid.	Deep violet, gradually turning brown.	Brown, with a slight violet tinge.
One drop of strong sulphuric acid was added to a solution of one drop of the oil in 1 c.c. of chloroform.	Violet-red tint, rapidly changing to rose-red, and finally to yellow-brown.	Green at first, becoming brown.
Two c.c. of a solution of sodium phospho-molybdate acidified with nitric acid were added to a solution of 1 c.c. of the oil in 5 c.c. of chloroform.	Blue-green.	Very faint bluish-green colour.
Ammonia was added to the preceding solution.	Intense blue.	Very pale blue.
Three drops of fuming nitric acid were cautiously added to about 10 drops of the oil.	Red at place of contact, changing to deep pink, and finally to yellowish-brown.	Yellow at place of contact changing to dirty violet colour.

Viscosity (Time of Efflux).—Fifty c.c. of spinacene required 78 seconds to flow through the aperture of a Redwood viscosimeter at 21° C., as compared with an average of 370 seconds for rape oil.

Absorption of Oxygen.—1.662 gm.s. of spinacene were exposed in a flat bottomed glass dish to an atmosphere of oxygen at the ordinary temperature. At the end of two months the hydrocarbon had absorbed 0.397 grm. of oxygen, and had become so viscous that it would not flow. Thin films of the hydrocarbon when exposed to the air formed a hard skin similar to that given by linseed oil.

Whether regarded from the analytical or from the physiological point of view, the existence of fish-liver oils containing nearly 90 per cent of an unsaturated hydrocarbon as a normal constituent is a matter of considerable interest and importance.

At first it appeared to be just possible, notwithstanding M. S. Baum's results, that the fish from which the oil was obtained were in some way or other abnormal. The fact that samples of oil having approximately the same composition were derived from fish which had been caught during periods extending over several weeks, and that the consignments represented by the sample submitted to me amounted to nearly 5000 litres, appeared, however, to negative any suggestion of abnormality. A paper by M. Tsujimoto (*J. Ind. Eng. Chem.*, 1916, viii., 889), which I have only quite recently seen, seems finally to settle this point, since he has obtained from the livers of certain Japanese sharks a hydrocarbon to which he has given the name "squaline," which resembles spinacene very closely, and may prove to be identical with it.

The presence of hydrocarbons in fatty oils is probably of much more frequent occurrence than has hitherto been supposed, and there can be little doubt that the unsaponifiable matters other than cholesterol, phytosterol, and similar alcohols, often consist mainly of these substances. It is well known that fish-liver oils frequently contain somewhat high percentages of unsaponifiable matters, and this would appear to be particularly the case with shark-liver oil, which, according to Lewkowitsch, may contain over 20 per cent of such substances stated to consist chiefly of cholesterol.

In view of the results recorded in this paper, it is of considerable interest to note that Allen ("Commercial Organic Analysis," vol. ii., part i., p. 201) gives the following results for four samples of oil which he refers to as "presumably adulterated shark oil"—

	A.	B.	C.	African fish oil.
Sp. gr. at 15.5° C.	0.8746	0.8992	0.8661	0.8672
Percentage of KOH required	—	4.50	5.50	—
Ether-residue	69.9	80.8	83.5	82.8

Allen says: "The ether-residue was generally of a bright yellow colour, like the original oil, remained quite clear on cooling, and volatilised somewhat readily. A further ex-

amination was made of the ether-residue from sample B, which was free from nitrogen and nearly free from oxygen. It gave, when heated, an unmistakable odour of pine resin, and appeared to be a mixture of light rosin oil with shale or petroleum lubricating oil. With concentrated sulphuric acid, B gave a reddish-brown coloration, becoming darker on stirring."

Allen also says: "Owing to frequent adulteration, the physical and chemical characters of shark oil have been mis-stated by many authorities. Thus it is commonly alleged to be of very low specific gravity, a character in all probability really due to the presence of a large proportion of mineral oil or similar adulterant, which addition caused the saponified sample to yield large ether-residue. Whether or not these oils of low specific gravity were uniformly adulterated is no longer of much practical interest, as oil of such character is not now to be met with."

There can now be very little doubt that the samples examined by Allen were not, as he suspected, adulterated oils, but were samples of genuine oil obtained from certain of the *Squalidae* or *Spinacidae*, and consisting largely of spinacene or some similar hydrocarbon.

In 1906, Tsujimoto published in the *Journal of Chemical Industry* of Tokyo an account of a sample of oil obtained from the liver of a Japanese shark containing 56.1 per cent of unsaponifiable matters consisting mainly of an unsaturated hydrocarbon, to which at that time he assigned the formula $C_{10}H_{18}$. In his recently-published paper, to which I have referred above, he deals with the oil obtained from the livers of two species of Japanese shark which contained from 70 to 90 per cent of an unsaturated hydrocarbon.

Inasmuch as the existence of shark-liver oils containing such high proportions of unsaponifiable matter is now thoroughly well established, it is clear that the standards given in many textbooks will need to be very considerably revised, and that the analyst will have to proceed with caution when asked to pronounce an opinion as to the genuineness or otherwise of a sample of such oil.

Thus, Lewkowitsch ("Chemical Technology and Analysis of Oils, Fats, and Waxes," vol. ii., table facing p. 370) gives for Arctic and Japan Shark Oils numbers for the specific gravity at 15°/15° C. ranging from 0.9105 to 0.9177, while Allen records numbers ranging from 0.9185 to 0.9285. On the other hand, shark-liver oils consisting largely of hydrocarbon such as those referred to in this paper have a specific gravity at 15°/15° C. of 0.86 to 0.88, and it is not improbable that genuine oils having intermediate specific gravities may occur.

For the iodine value, numbers are given by Lewkowitsch varying from 137 to 162, while Hunt (*J. Soc. Chem. Ind.*, 1902, xxi., 455) gives a mean of 98.9. The hydrocarbon-containing oil, on the other hand, gives numbers in the neighbourhood of 360.

Again, whilst ordinary shark-liver oil gives about 20 to 25 per cent of a bromide compound insoluble in ether, the hydrocarbon-containing oil yields as much as 76 per cent.

If, as the result of further experience, it should be found that all shark-liver oils are capable of being divided more or less sharply into two classes—namely, those which consist mainly of glycerides and those which consist mainly of unsaturated hydrocarbons—the position of the analyst will be tolerably clear; but if, as seems more probable, there is a more or less regular gradation from one class to the other, then it will become very difficult to express a definite opinion as to whether a given sample consists of genuine shark liver oil or not.

It is obvious, moreover, that a question will be asked which may not be very easy to answer—namely, what is shark-liver oil? It is very clear that, since the two classes of liver oil to which I have referred are very different products, usable for different purposes and probably commanding different prices, shark oil will in all cases have to be bought and sold on the results of analysis.

The spinacene-containing oil can be very readily distinguished from fish-liver oil adulterated by the addition of added hydrocarbons by the high iodine value of the unsaponifiable matter and by the large amount of ether-insoluble bromide formed when it is treated with bromine.

So far as the unsaponifiable matter is concerned, it should be borne in mind that oils of the high specific gravity class containing up to 25 per cent of unsaponifiable matters are often met with, the unsaponifiable matter in this case consisting largely of alcoholic bodies such as cholesterol.

It was thought that it would be of interest to compare the colour reactions given by the fish-liver oil containing spinacene with those given by an average sample of cod-liver oil. The results are given in Table A.

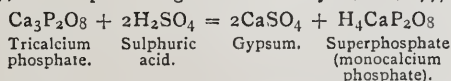
Spinacene itself does not give any of the above reactions. As might be expected, therefore, the spinacene-containing oil gives the various colour reactions much more faintly than ordinary liver oils.

With regard to the uses to which spinacene, or fish-liver oils containing large proportions of it, may be put, it is too soon to express any opinion, since this can only be determined by experiments on a fairly large scale. It may, however, be permissible to utter a note of warning, since oils containing any considerable proportion of this hydrocarbon would be liable to oxidise with considerable readiness and might be very dangerous if used for such purposes as, for example, the oiling of wool in the manufacture of woollen goods. In this connection I might refer to a note recently published by Fairley and Burrell (*J. Soc. Chem. Ind.*, 1917, xxxvi., 113), although the oil in that case consisted largely of fatty acids, and could not have contained spinacene.—*The Analyst*, May, 1917.

SOME FACTORS INFLUENCING THE SOLUBILITY OF PHOSPHORIC OXIDE IN MIXED FERTILISERS CONTAINING SUPERPHOSPHATES.

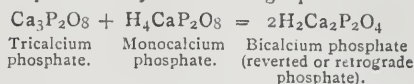
By EDMUND VICTOR FLACK.

SUPERPHOSPHATES are produced by treating bones or phosphatic minerals with sulphuric acid. The reactions which take place may be summarised as follows (H. W. Wiley, "Principles of Agricultural Analysis," ii., 277):—

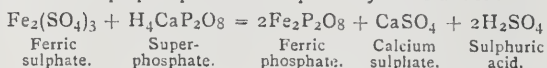


It is well known that the water-soluble phosphoric oxide content of superphosphate gradually decreases in amount, and this decrease is known as "reversion" or "retrogression." The longer the superphosphate is kept the greater will be the amount of reversion, and the rate of reversion varies with the process of manufacture. In some superphosphates there may be practically no reversion, whereas

in a badly-made article, in which unsuitable materials have been employed, it may be considerable. Thus a mineral containing more than 10 per cent calcium carbonate, 3 per cent of oxide of iron and fluorides, would be very unsuitable (*Bull. Imperial Institute*, ix., [1]). Insufficiency of acid in the material used for preparation also causes considerable reversion. Such reversion may be due to any undecomposed tricalcium phosphate, or to calcium carbonate, iron oxide, or alumina in the mixture acting on the water-soluble phosphate. In the case of the first-mentioned compound the reaction may possibly be very slight, and would be represented by the following equation:—

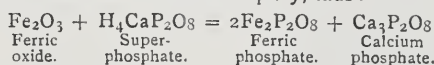


When iron is present as pyrites or ferric silicate in the mineral used, there is no reversion, but when present as ferric or ferrous oxide, the reversion is great. What actually takes place is not so clear as when tricalcium phosphate is present. If the acid used had dissolved a quantity of iron the reaction of the resulting ferric sulphate with the superphosphate would probably be as under:—



The sulphuric acid thus set free would dissolve more of the iron compounds, and so react again and again. In this case we have a continuously increasing quantity of insoluble iron phosphate, and a proportionately diminishing amount of soluble phosphates (Aikman "Manures and Manuring," Second Impression, 399).

On the other hand, the soluble phosphates may be rendered insoluble much more rapidly, thus:—



The above would apply in the case of alumina as well as for iron compounds.

But the solubility of the phosphoric oxide in superphosphate is influenced by other factors than merely calcium carbonate, tricalcium phosphate, and compounds of iron and alumina. To test the extent to which this solubility is affected the following mixtures were prepared:

- (a) Superphosphate and sulphate of ammonia.
- (b) Superphosphate and sulphate of potash.
- (c) Superphosphate and kainit.
- (d) Superphosphate and guano from the Union Government Islands off the South African coast.
- (e) Superphosphate and bone meal.

In the *Cape Agricultural Journal* of June, 1910, there was published a diagram—stated to have been compiled on experience and practice in South Africa—showing what artificial fertilisers could be mixed together without any harmful effects, and what were the mixtures best suited for the farmer.

On consulting this diagram it will be seen that the mixtures made by me were those there specially recommended to be made by farmers, with the exception of (e), the mixture of superphosphate with bone meal, a combination marked as unnecessary, although sometimes made use of by farmers.

The above mixtures were made to contain equal parts by weight of each of the two constituents; these were well mixed, and at once placed in glass bottles, closed by means of corks, and the portions were weighed out after the mixture had stood for the required time. Before each weighing the sample was again well mixed.

The sample of superphosphate used throughout the first part of these experiments was a high-grade article containing 17.35 per cent of water-soluble phosphoric oxide and 26.92 per cent of lime.

The guano used represented the average article as sold by the Union Government. It was a mixture from

Malagas, Marcus, and Jutten Islands, and had the following composition:—

	Per cent.
Material capable of passing through a 1 mm. sieve	93.66
Phosphoric oxide—	
Total	13.80
Citrate-soluble	13.47
Water-soluble	4.11
Lime	12.49
Potash	1.69
Nitrogen	10.94

The methods adopted for analysing these mixtures were as follows:—

20 grms. of the fertiliser were extracted with distilled water for half-an-hour in a shaking machine, filled up to 1000 cc., well mixed, and filtered. In an aliquot part of the filtrate the water-soluble phosphoric oxide was precipitated direct by means of ammonium citrate and magnesium mixture in the ordinary way.

By this method each of the five mixtures was analysed after standing for three hours, for twenty-four hours, one week, two weeks, and three weeks, thorough mixture, as already stated, being again made before each testing. The percentages of water-soluble phosphoric oxide were thus found in the various mixtures are given in Table I.

TABLE I.

	Original composition.	Composition after standing for—				
		3 hrs.	24 hrs.	1 week.	2 weeks.	3 weeks.
Superphosphate alone	17.35	—	—	—	—	—
(a) Superphosphate and sulphate of ammonia ..	8.68	8.58	8.67	8.71	8.79	8.89
(b) Superphosphate and sulphate of potash	8.68	8.65	8.65	8.65	8.74	8.64
(c) Superphosphate and kainit ..	8.68	8.62	8.76	8.62	8.76	8.69
(d) Superphosphate and Government guano ..	10.73	10.00	9.54	9.22	9.08	8.47
(e) Superphosphate and bone-meal ..	8.68	8.49	8.52	7.82	7.41	—

The first column of figures shows the calculated amounts of water-soluble phosphoric oxide in the mixtures, the other columns being obtained, as already stated, by direct analysis.

For comparison I append a series of results obtained by Prof. G. Gray, of the Canterbury Agricultural College, Lincoln, New Zealand (*Trans. Australasian Assoc. for the Advanc. of Sci.*, Dunedin, 1904), from mixtures made up on similar lines to those above mentioned, and also consisting of equal parts of their respective constituents (Table II.).

TABLE II.

	Original composition.	Composition after standing for—				
		3 hrs.	24 hrs.	6 days.	12 days.	18 days.
Superphosphate alone	17.74	—	—	—	—	—
1. Superphosphate and kainit ..	8.87	8.87	8.87	8.50	8.25	8.25
2. Superphosphate and Coral Queen guano ..	8.87	8.87	8.57	8.37	8.37	8.25
3. Superphosphate and Chesterfield guano ..	8.87	7.87	7.37	4.87	4.00	3.37
4. Superphosphate and bone-dust ..	8.87	8.87	8.87	8.87	8.62	8.62

The guanos used by Prof. Gray for his mixtures had the following percentage composition:—

	Coral Queen.	Chesterfield.
Citrate-soluble phosphoric oxide	18.5	17.5
Calcium carbonate	1.1	37.9
Iron oxide	8.8	—

Table III. shows the total percentage change in each of the mixtures during the periods specified:—

TABLE III.

	3 hours.	24 hours.	1 week.	2 weeks.	3 weeks.
(a) Superphosphate and sulphate of ammonia	-1.15	-0.11	+0.35	+1.27	+2.42
(b) Superphosphate and sulphate of potash	-0.35	-0.35	-0.35	+0.69	+0.46
(c) Superphosphate and kainit ..	-0.69	+0.92	+0.69	+0.92	+0.12
(d) Superphosphate and Government guano ..	-6.80	-11.09	-14.07	-15.37	-21.06
(e) Superphosphate and bone-meal	-2.18	-1.84	-9.90	-14.63	—

In Table III. a minus sign shows reversion, and a plus sign indicates an increase upon the original amount of soluble phosphoric oxide. In Prof. Gray's experiments there was reversion in every case, and the percentages of the original water-soluble phosphoric oxide reverted are shown in Table IV.

TABLE IV.

	3 hrs.	24 hrs.	6 days.	12 days.	18 days.
1. Superphosphate and kainit ..	0.0	0.0	-4.1	-6.9	-6.9
2. Superphosphate and Coral Queen guano ..	0.0	-3.3	-5.3	-5.3	-7.0
3. Superphosphate and Chesterfield guano ..	-11.2	-16.9	-44.8	-54.9	-62.0
4. Superphosphate and bone-dust ..	0.0	0.0	0.0	-2.8	-2.8

The tabulated results of my analyses show that the greatest reversion took place in mixture (d), superphosphate and Government guano, and that in this respect the superphosphate bone-meal mixture (e) was not far behind.

The results obtained from mixture (a), superphosphate and sulphate of ammonia, are of great interest, in that they showed, after the first week, a very slight but decided increase in water-soluble phosphoric oxide. A further set of experiments was conducted to ascertain whether this slight increase of the water-soluble phosphates in mixture (a) could be accounted for. A high-grade superphosphate (manufactured in Japan) containing 19.37 per cent of water-soluble and 20.39 per cent of total phosphoric oxide, and a total of 28.03 per cent of combined lime, was employed in this and all subsequent work, and the tests were carried out on similar lines to those already detailed. The sulphate of ammonia employed in this set of analyses was the chemically pure salt, not the commercial article as usually sold for fertilising purposes, which was employed in the previous experiment. The results obtained are as follows:—

Original mixture	9.685
Three hours	9.48
Twenty-four hours	9.48
One week	9.67
Two weeks	9.66
Four weeks	9.65

Here, again, as in the case of mixture (a), it will be seen that a similar drop in solubility took place within a few hours, from which there was a recovery after the mixture had stood for one week. The increase in solubility noticed in the previous experiment did not occur.

When, however, our attention is turned to the Government guano mixture (d), it will be seen that the actual loss of water-soluble phosphates is 21 per cent of the amount originally present. It appeared likely that the large amount of ammonium salt, existing probably as ammonium carbonate in the guano, would account for the high percentage of reversion. So the experiment detailed hereunder was carried out.

Ammonium carbonate—extra pure—was freed from adherent moisture by extracting first with absolute alcohol. The alcohol was allowed to drain off, and the residue then taken up with chemically pure ether. The ether was allowed to evaporate off in the sun, the residual carbonate was then powdered, and after sifting through a 1 mm. sieve it was mixed with an equal weight of superphosphate. This mixture was placed in a glass stoppered bottle, and the gas (carbon dioxide) was driven off rapidly by the action of the acid of the superphosphate. After standing as in previous experiment the following percentages of water-soluble phosphoric oxide were obtained:—

Original mixture	9.685
Three hours	2.58
Twenty-four hours	0.78
One week	0.42
Two weeks	0.47
Four weeks	0.42

Clearly, therefore, the considerable decrease of solubility when superphosphates are mixed with Government guano is due to the presence of ammonium carbonate in the guano.

In the case of kainit, Gray remarks that this reversion may be put down mainly to magnesium salt. The most interesting mixture of all is that of superphosphate and bone-meal in the above mixtures prepared by me; the reversion had amounted to over 14½ per cent in two weeks. In Gray's experiment only 3 per cent of the soluble phosphoric oxide reverted.

In a further experiment bone-ash, $\text{Ca}_3\text{P}_2\text{O}_8$, was used, which was found to contain 0.74 per cent of soluble phosphoric oxide. (A duplicate determination gave 0.73 per cent). The superphosphate was the same as previously used, analysing 19.37 per cent of water-soluble phosphoric oxide.

This mixture (equal parts of bone-ash and superphosphate) gave the following percentages of water-soluble phosphoric oxide at the end of the times stated:—

Original mixture	10.05
Three hours	12.05
Twenty-four hours	12.10
One week	11.65
Two weeks	11.59
Four weeks	11.24

The figures obtained from the first two determinations were rather surprising, and as they might possibly have been due to improper mixing a further independent mixture was made, which analysed 12.14 and 12.09 after standing for three and twenty-four hours respectively.

This increase was plainly due to the presence of free acid in the superphosphates used in the above set of experiments; or, in other words, there was enough free acid in the superphosphate used to bring about solution of the 2.00 per cent of phosphoric oxide by which the original 10.05 per cent was increased. In order to confirm this a solution of a superphosphate was made as follows:—100 grms. were extracted for half-an-hour with distilled water in a 1000 cc. flask, shaken in a shaking apparatus for half-an-hour, filled up to the mark, and an aliquot part of the filtrate gave a result equivalent to 18.92 per cent of water-soluble phosphoric oxide in the superphosphate.

To 500 cc. of the clear filtrate, equivalent to 50 grms. of superphosphate, 3.35 grms. of pure precipitated tricalcium phosphate were added, and the mixture extracted in a shaking apparatus for half-an hour, filled up to the 1000 cc. mark, well mixed, and filtered. In an aliquot part the water-soluble phosphoric oxide was found to be equivalent to 19.84 per cent, again proving that in the mixture of superphosphate and bone-ash an increase in the water-soluble phosphoric oxide results.

A blank determination of the water-soluble phosphoric oxide in the quantity of precipitated tricalcium phosphate actually used was found to yield 0.064 gm. of water-soluble phosphoric oxide.

	Per cent.
Calculated amount in a mixture of 100 grms. of superphosphate and 6.70 grms. of precipitated tricalcium phosphate	17.90
Percentage found in a mixture of 100 grms. of superphosphate and 6.70 grms. of precipitated tricalcium phosphate after shaking	19.84

A further test, using some specially prepared $\text{Ca}_3\text{P}_2\text{O}_8$ from Kahlbaum, containing 0.0256 gm. of water-soluble phosphoric oxide, gave the following results:—

Calculated amount (per cent)	17.78
Percentage found after shaking (per cent)	20.23

In order to confirm the above the following mixture were made:—

- A medium high-grade superphosphate and bone-ash containing 15.63 per cent and 0.73 per cent of water-soluble phosphoric oxide respectively.
- A high-grade superphosphate and bone-ash containing 18.25 per cent and 0.65 per cent of water-soluble phosphoric oxide respectively.

The results of the analyses being:—

	A.	B.
Original mixture	8.18	9.45
Three hours	9.65	10.04
Twenty four hours	9.39	9.94
One week	8.89	—
Two weeks	8.66	—
Three weeks	8.86	—
Four weeks	8.80	—

This once more proves that an increase of water-soluble phosphoric oxide results when superphosphate and bone-ash are mixed.

In order to confirm the above results and ascertain if there would be such an increase when weighed quantities of calcium phosphate of different origin are extracted with a water solution of superphosphate, the following quantities were taken:—

- 4.366 grms. of pure calcium phosphate.
- 4.366 grms. of bone-ash.
- 4.366 grms. of precipitated calcium phosphate.

These were all treated in the same manner, the quantity being extracted for half-an-hour in a shaking machine with 500 cc. of superphosphate solution, then filtered, and in an aliquot part the water soluble phosphoric oxide was determined, the results being:—

	A.	B.	C.
Theoretical amount of water-soluble phosphoric oxide (per cent)	16.81	16.83	16.93
Percentage of water-soluble phosphoric oxide found (per cent)	17.59 (a)	17.82	17.89

- This result was obtained by extracting the 4.366 grms. with 500 cc. of superphosphate solution, as already described, taking an aliquot part (equivalent to 2 grms.) for analysis. The determination was repeated a second and third time with similar quantities of material, viz., 4.366 grms. of calcium phosphate were extracted with 500 cc. of super

phosphate solution, but the mixture was diluted to 1000 cc.; larger aliquot parts, corresponding to a $2\frac{1}{2}$ grms. and a 1 gm. quantity respectively, were taken for analysis, and gave 17.96 per cent and 17.87 per cent of water-soluble phosphoric oxide.

In the first line the figure given is the calculated amount of water-soluble phosphoric oxide in a mixture of 100 grms. of superphosphate, and 8.732 grms. of the calcium phosphate, and in the second line the percentage of water-soluble phosphoric oxide after shaking for half-an-hour in a shaking machine.

The quantity of material used, 4.366 grms., gave the following amounts of water-soluble phosphoric oxide:—

No.	Material.	Weight of soluble phosphoric oxide (gm.).
A.	Pure calcium phosphate	0.0164
B.	Bone-ash	0.0284
C.	Precipitated tricalcium phosphate..	0.0793

Conclusions.

Superphosphate can remain mixed for as long as three weeks with either sulphate of ammonia or sulphate of potash or kainit without an appreciable loss of water-soluble phosphoric oxide, and if mixed with sulphate of ammonia there is a possibility of an actual increase of water-soluble phosphoric oxide in a period of three weeks.

If immediate reversion of water-soluble phosphoric oxide is to be avoided Government guano should on no account be mixed with superphosphate, for in a mixture of equal parts of the two there is, even after three hours, a total loss of nearly 7 per cent of the water-soluble phosphoric oxide.

In the case of bone-meal there is a loss of 2 per cent of water-soluble phosphoric oxide in three hours, but if left for a period of fourteen days there is considerable loss, amounting to over $14\frac{1}{2}$ per cent.

It is quite evident that the two samples of kainit as used by Gray and myself varied considerably, judging from the loss of water-soluble phosphoric oxide; the substance used by the former caused a loss of nearly 7 per cent in eighteen days, whereas in my case there was a slight increase of water-soluble phosphoric oxide. These remarks apply also to the two bone products used; in the former case there was a loss of only $2\frac{1}{2}$ per cent in eighteen days, as against $14\frac{1}{2}$ per cent in fourteen days with the substance used by me.—*South African Journal of Science*, xlii., No. 5.

ATTEMPT TO SEPARATE THE ISOTOPIC FORMS OF LEAD BY FRACTIONAL CRYSTALLISATION.*

By THEODORE W. RICHARDS and NORRIS F. HALL.

(Concluded from p. 283).

Purification.

BECAUSE of the smallness of the end fractions it was necessary to unite several to obtain a sufficient quantity of material for purification.

(NOTE.—This action nullified the effect of 19 crystallisations on the more soluble end and 83 crystallisations on the less soluble end. Thus the total number of effective crystallisations was 904. The mother-liquor on the less soluble end resulted from an average of 71 tiers of successive products, and on the more soluble end from an average of 65 tiers. It is to be regretted that this reduction in the efficiency of the process was rendered necessary by the small yields at the two ends of the line, but enough crystallisations remained effective to test the question at issue, at least in a preliminary way).

From the mother-liquor, or "more soluble" end Fractions 989–992 were taken, united, and called Sample A. Sample B was made up of Fractions 999–1006 from the crystal, or "less soluble" end. From this point on the two samples were treated in an identical manner. Chiefly to remove the large amount of silica which had dissolved from the casseroles during the fractionation, the crystals were first electrolysed in warm concentrated solution between platinum wires. The well-formed flat leaflets of lead were removed from time to time with a glass rod, rinsed with a stream from a wash-bottle, and preserved in quartz dishes until all the metal had been deposited from the solution. The crystals were further washed from time to time, and all washings returned to the electrolysis bath, which was gradually reduced in volume as the concentration of lead became smaller. The lead crystals were then dissolved in a nitric acid made by diluting with the purest three times distilled water, nitric acid which had itself been distilled through a platinum condenser with rejection of the first third. The excess of acid was evaporated, and the crystals of lead nitrate dissolved in the purest water, filtered through a platinum Gooch crucible, and precipitated by the addition of a large excess of redistilled nitric acid, and cooling with ice. The crystal meal thus obtained was freed from adhering acid in the platinum centrifuge, washed centrifugally with purest concentrated acid, and redissolved in the least possible amount of pure boiling water.

Five precipitations with centrifugal drying were made in this way. The crystals from the fifth crystallisation were placed in a quartz dish and dissolved. From this solution lead chloride was precipitated by passing in pure hydrochloric acid gas made by warming the purest acid of commerce. The chloride thus obtained was dried in the centrifuge, washed with cold water, and redissolved in boiling water. Four crystallisations as chloride followed. A little hydrochloric acid was added to the solution each time to prevent the formation of basic salt and to render the chloride less soluble. The last crystals, after centrifugal washing and drying, were preserved in an exhausted desiccator over fused potash. Nothing but platinum and quartz vessels were used.

The Determination of Atomic Weight.

For these determinations the usual procedure was employed. About 5 grms. of the dried crystals were placed in a platinum boat, which with its container had been carefully weighed. The boat was gradually heated in a quartz tube attached to the usual "bottling apparatus," in a current of pure dry hydrochloric acid gas. After nearly all the residual water had been driven from the crystals the temperature was raised so as to fuse the salt, which was then cooled as quickly as possible in a current of pure dry nitrogen prepared by the Wanklyn process.

Mayer (*Phys. Review*, 1915, vi., 288) has shown that against an excess of pressure (such as was always maintained within our tube) no oxygen diffuses through a layer of quartz even as thin as 0.5 mm., and our tube walls were 2.5 mm. thick. (Incidentally it may be noted that Mayer's interesting results seem to indicate that when diffusion takes place it is rather of the nature of transpiration through actual holes than solid solution—for in the latter case small difference of pressure would make far less difference than he observed). This observation is confirmed by our experience. The hydrochloric acid delivered from the end of the tube dissolves in water without visible residue (indicating the absence of more than a trace of any slightly soluble gaseous impurity), and very rarely was there any significant corrosion of the boat, which would have occurred with only a trace of oxygen. Only once when the salt was kept fused a long time its brownish colour on cooling showed that a little platinum had dissolved. This sample was, of course, rejected. The delicacy of this colour test is shown by the weights of the boat before and after this fusion which differed only by 0.24 mgrm., although the salt was distinctly brown. No

* *Journal of the American Chemical Society*, xxxix., No. 4.

trace of colour was observed in any other case, nor was the loss of weight of the boat otherwise over 0.09 mgrm.

After the salt had cooled and the nitrogen had been replaced by dry air the boat was pushed into the weighing tube, bottled, and reweighed.

The boat and salt were next heated at 80–90° on an electric stove in a glass flask containing about a litre of water to which enough pure nitric acid had been added to prevent the formation of basic salt, until the lead chloride had all dissolved. One sample boiled for a few minutes, and was rejected at once for fear that a trace of the salt had been carried out by spray. As usual (Richards and Wadsworth, *Journ. Am. Chem. Soc.*, 1916, xxxviii., 2616), a small amount of siliceous and carbonaceous residue had to be removed by scrupulously quantitative filtration through a tared Gooch-Monroe crucible. On the average, about twice as much was found in the more soluble fraction as in the other. The weight thus removed was subtracted from the weight of the fused salt. Before filtration the boat had been carefully lifted out and thoroughly washed, and the filtrate was collected in the precipitating flask.

A supposedly equivalent weight of silver was next dissolved in pure nitric acid mixed with an equal bulk of water in a flask with a chain of bulbs ground into the neck, a steam-bath being used to heat the solution. More water was then added, and the temperature raised until a few seconds' gentle boiling had removed nitrous fumes. The solution having been made up to a litre it was added very slowly with constant agitation to the lead chloride solution. Actinic light was henceforth rigorously excluded from the precipitated silver chloride. The precipitate was coagulated by violent shaking, usually for fifteen minutes, and allowed to stand at least twenty-four hours, with further occasional shakings before samples were removed for tests. The end-point was found by the customary method by means of the nephelometer, and tested for several days to be certain that it did not change.

Vacuum corrections were applied as usual, and all customary precautions were taken.

Previous to this work two analyses of ordinary lead had been made. (The fused chloride made from this lead contained no perceptible trace of insoluble residue).

TABLE I.

Analysis.	Sample.	PbCl ₂ corr. to vacuum.	Ag corr. to vacuum.	Ratio PbCl ₂ :Ag.	At. wt. Pb.
The Atomic Weight of Ordinary Lead.					
1.	Pb	7.13723	5.53723	1.28895	207.187
2.	Pb	7.60063	5.89675	1.28895	207.186
Average					207.187
Atomic Weight of End Fractions of Isotopic Lead.					
7.	A	3.70016	2.87854	1.28543	206.426
9.	A	4.79633	3.73154	1.28535	206.409
14.	A	4.64577	3.61412	1.28545	206.431
Average					206.422
10.	B	4.64736	3.61568	1.28534	206.406
11.	B	4.87838	3.79519	1.28541	206.422
15.	B	4.68396	3.64425	1.28530	206.399
Average					206.409
Ag = 107.880. Cl = 35.459					

Table I. includes all the analyses of the materials which were completed; any which had become the object of suspicion were rejected at an early stage.

Obviously, if the fractional crystallisations produced any change in the relative concentrations of radium G and lead this change is very small. The means of the two series of determinations of isotopic lead differ only by about 6 parts in 100,000. This is certainly within the

bounds of possible experimental error, though the low "average errors" of the two sets (0.008 unit in each case) tempt one to assign a meaning to the observed difference. At any rate, we are safe in concluding that assuming the atomic weights of radium G and lead to be 206.6 and 207.2 respectively, no change in concentration greater than 13,1200 or 1.1 per cent has been obtained by 900 crystallisations. Even supposing that a real difference in solubility exists, and making the further conservative assumption that the bunching of the end fractions reduced the effect of the crystallisation by one-fifth it is evident that complete separation could not be attained in less than 70,000 fractionations. It is interesting to note again that the average amount of residue in the "more soluble" Fraction B, which must have contained a far larger original siliceous impurity, was 2.3 times as large as that in the "less soluble" Fraction A, and B is also the one which shows the lower atomic weight. This is confirmatory of the experience of Richards and Wadsworth (*loc. cit.*), who say:—"It is noticeable that in general those preparations which contained appreciable amounts of the residue were slightly lower than the others as regards the final atomic weight obtained." Perhaps a trace of basic salt is carried away with the residue, thus causing its actual weight to be too great, and because the actual weight is subtracted from the total lead chloride, the apparent atomic weight of lead would consequently be too low. In that case the slight difference between Series A and B might be attributed to experimental error from this cause. The matter will receive further attention; in any case it does not seriously affect the conclusion.

Estimation of Radio-activity.

The β -ray activity of the lead used indicates that it contains, in about 3 parts so-called "radium G" and 1 part lead, an amount of "radium D" of the order of 10–7 parts. This is betrayed by the steady growth of a penetrating β -ray product ("RaE") which comes to practical equilibrium with its parent in about a month after they are separated. Evidently the ionisation, if the α -rays from the polonium present are cut off, caused by a weighed amount of the material under constant conditions, is a measure of the concentration of radium D relative to its isotopes "radium G" and lead. Thus the determination of the activity of the end fractions gives information as to the relation between the solubility of the nitrate of radium D and the mean solubility of the nitrates of radium G and ordinary lead, a relation of great interest because it cannot be tested by atomic weight determinations, and because the difference between the theoretical atomic weight of radium D and that found for the mixture is $210 - 206.4 = 3.6$, or three times as large as that between radium G and lead. Any difference in the properties of isotopes might naturally be expected to be greater the greater the difference between the atomic weights; hence this case should afford an especially favourable test of the theory of complete identity.

The method was as follows:—To eliminate differences in moisture content, and consequently in absorptive power, the two samples were kept in the same exhausted desiccator after purification. When sixty-six days had elapsed 10.25 ± 0.03 grms. of each sample were weighed into a marked metal dish and tamped with a platinum spatula. The material formed a layer of thickness defined by the expression 0.88 gm./cm^2 . This is far too thin to give a maximum ionisation due to the complete absorption of the β -rays from the lowest layers, but is thick enough so that no great accidental changes in thickness needed to be feared, and the effect of small changes was annulled as described below. The dishes were covered in turn with the same thin sheet of paper and introduced into a grounded aluminium-leaf electroscope which was very kindly loaned by Prof. William Duane. The rate of fall of the leaf was then observed with a stopwatch in the usual manner. The position of maximum sensitiveness was ascertained by preliminary experiments,

and the telescope adjusted to this position. The leaf was then always charged to such a potential that it was at the same division of the scale at the beginning of each measurement. The time taken for it to reach another division on the scale (always the same one) was then noted. By this means all errors arising from differences of potential, differences of stiffness of the leaf in different positions, and inhomogeneity of the scale were at once eliminated. The leaf was charged first to an indefinite potential higher than that desired, then by means of an active preparation of polonium held near the base of the electroscope, it was quickly discharged to a point a few scale divisions above the initial mark, and its slow passage across this mark was then observed at leisure. The two dishes were introduced alternately into the electroscope to eliminate the effect of changes in the natural leak, and were thoroughly stirred and repacked between every two measurements to allow for small accidental differences in thickness. The dish not in use was removed always to the same position at a distance from the electroscope and heavily screened so that no variation in the amount of radiation from this source could affect the rate of fall. The electroscope was carefully screened from all other radio-active material and from neighbouring sources of X-rays. Illumination was secured from a tungsten filament lamp at a considerable distance from the leaf, and any convection currents caused in the gas inside the electroscope-case by radiation from this source must certainly have reached a steady state before the work was begun.

These somewhat elaborate precautions are discussed in detail, because it was not until many preliminary experiments had shown the necessity of observing them that a satisfactory degree of reproducibility was obtained. Thanks are due to Drs. David L. Webster and Harry Clark for much kindly suggestion and assistance.

It is believed that Table II., which includes all the observations affected by no known source of error, represents about as good reproducibility as this electroscope can be made to give. The chief difficulty is in focussing so sharply on the edge of the leaf that the precise instant of its passage of any scale division can be exactly estimated.

TABLE II.

Sample A.	Sample B.
11.30	11.32
11.43	11.62
11.69	12.06
11.56	11.43
11.61	11.70
11.47	11.34
11.49	11.32
11.50	11.43
11.41	11.47
11.58	11.36
Averages .. 11.504	11.505

The ionisation is expressed in arbitrary units (scale divisions per minute). The natural leak (which must have been the same for both as they were taken alternately) was found to be 0.50 ± 0.01 . The agreement of the means to 1 part in 10,000 must be regarded as fortuitous, since their mean probable error is about 0.11 unit. This error, divided by the mean value from which has been subtracted the natural leak, is a measure of the accuracy of the determination. Its value is $\frac{11}{1150-50} = \frac{1}{100}$. This

work definitely shows, then, that no change in the relative concentration of radium D and its isotopes as great as 1 per cent has occurred in 900 fractionations, and certainly gives no indication that even a smaller change has occurred. In other words, making the same conservative assumption as before, we have proof here that radium D cannot be completely separated from its isotopes by this method in less than 80,000 crystallisations.

If ordinary lead is a mixture of isotopes this mixture must have been made very long ago while the earth was still in a highly mobile condition, since all the ordinary lead throughout the world seems to have the same atomic weight (Baxter and Grover, *Journ. Am. Chem. Soc.*, 1915, xxxvii., 1058). Could the composite nature of ordinary lead be proved the identity of the several samples through geological aeons would form another argument in favour of the inseparability of the constituents.

To the Carnegie Institution of Washington we are greatly indebted for some of the apparatus and material used in this research, which is to be continued in the near future.

Summary.

Lead from Australian carnotite (believed to contain about 1 part of ordinary lead to 3 parts of radium G, with a mere trace of radium B) has been fractionally crystallised over one thousand times as nitrate, and the end-fractions purified.

The atomic weights of the samples so obtained from the crystal and the mother-liquor ends of the series, respectively, agreed within the experimental error of 6 parts in 100,000.

The β -ray activities agreed within the experimental error of 1 per cent.

These observations indicate that the nitrates of radium D and lead, on the one hand, and radium B and lead, on the other hand, could hardly be separated, if at all, by less than 100,000 crystallisations.

Hence one might infer that the molal solubilities of the nitrates are probably essentially identical. The outcome gives strong experimental support for the hypothesis that isotopes are really inseparable by any such process as crystallisation.

NEW BRITISH DYE ENTERPRISE.

MOST MODERN GERMAN COLOURS TO BE MADE BY
FIRMS OF BIG CAPITAL.

(From a Correspondent).

It is possible now to obtain some idea of the line to be taken in the development of the new British coal-tar dye industry—more than half a century after the "epoch-making discoveries of Mr. Perkin" in this country.

Three undertakings which are run upon a considerable scale, with special devotion to research work—British Dyes, Ltd. (which has the financial backing of the Government), Messrs. L. B. Holliday and Co., of Huddersfield, and the Morton Sundour Fabrics, Ltd., Carlisle, at the present moment promoting a new company, Solway Dyes, Ltd.—have lately applied to the Patents Court for licence each to take, and manufacture under, eighteen German anthracene patents, and patents for anthraquinone derivatives, registered in the names of the Badische Anilin und Soda Fabrik, the Farbenfabriken vormals F. Bayer and Co., and the Farbwerke vorm Meister, Lucius, and Brüning. These patents are for brilliant fast blues, reds, browns, yellows, pinks, greens, olive, and orange vat dyes, and dating in registry to within about a year of the outbreak of war, mark the later milestones on the road Perkin opened up when he first derived "mauve" from aniline and magenta from a substance which has been put to more energetic uses lately—toluol!

In making their application on Friday (June 1), Mr. James Morton, Governing Director of the Morton Sundour Fabrics, Ltd., declared that his firm was the first to introduce indanthrene blue and alizarine saffron to the British market, at a time when there were none of these things outside Germany. It was harking back a long way to the first historic blues and yellows, when so much fuss was made over Perkin's *bleu de Lyon*, and a mild national panic was created by the disclosure that the yellow socks in vogue in that day contained picric acid. The Morton

Sundour Fabrics claim also to have been the first in the field with alizarine saffhrole, a fast blue dye for wool. Indeed, it is the "fastness" of their dyes which provides the firm with the second and rather unusual name in their title. Mr. Morton, making fabrics several years ago to sell on the attractive commercial guarantee of "a fresh supply gratis if the colour fades" had to eliminate all dyes which could not stand this searching test, and the firm, he announced, in this way more than any other, encouraged the German to produce the range of colours covered by these patents and gave them a permanent place on the market! Since the outbreak of the war Mr. Morton has been making "fast dyes" with the aid of ten chemists, and has, he said, spent £35,000 on experiments and plant, and is spending another £35,000 on new buildings and more plant.

The patents possess the following virtues:—

The first, 16,538 of 1904, makes violet-blue vat dyes by fusing benzanthrone (obtained from anthranol chlorine and sulphuric acid) with caustic alkali.

The second, 1818 of 1905, yellow-green vat dyes by forming the nitro-derivatives of the compounds produced under the first.

The third, 14,578 of 1905, is for the manufacture of derivatives of dianthraquinonyl, and their conversion into reddish yellow vat dyes by heating with caustic alkali.

No. 17,242 of 1905 is a blue dye in the form of chlor-indanthrene by heating indanthrene with antimony pentachloride.

A violet vat dye is given under 22,519 of 1905 by treating benzanthrone compounds with halogen or a halogenising agent.

A brown is 16,505 of 1907, by treating amido-derivatives of anthraquinone with a metal; say, copper in sulphuric acid solutions.

Blue, again, comes by treating (14,338 of 1908) indanthrene with a carbo-hydrate, such as grape-sugar, in the presence of an alkali, and brown (25,551 of 1908) by melting dianthraquinonyl 1.4-diamino-anthraquinones with caustic alkali.

2702 of 1909 is for the manufacture of benzoylamino-anthraquinones or derivatives thereof by treating amino-anthraquinones with acydlising agents capable of introducing the benzoyl radicle into the amino-groups, and 3055 of 1909 is for manufacture in the form of acydlised aminoanthraquinones by treating aminoanthraquinones or their derivatives with acydlising agents, and a process of dyeing and printing with these acydlised compounds.

Then come 7931 of 1909 for violet by treating with chlorine or bromide the vat dyes obtained by treating benzanthrone compounds with caustic alkali, and 24,486 1910 for the manufacture of 1.1-dianthraquinonyl-2.2-dialdehyde and its conversion into reddish yellow by treating with a condensing agent.

The rest are for intermediates—the principal, 894 of 1911, by condensing 1-nitro or 1-halogen anthraquinone 2-carboxylic acid with an arylamino body, and its conversion into red by further treatment with a condensing agent.

21,710 of 1911, intermediate in the form of amino-anthraquinones by treating an anthraquinone sulphonic acid with aqueous ammonia in the presence of an oxidising agent.

12,619 of 1912 (improvements in the manufacture of quinizarine), manufacture of intermediate quinizarine by condensing parachlorophenol with phthalic anhydride by means of concentrated sulphonic acid.

25,855 of 1912, manufacture of intermediates in the form of nitro-amino derivatives of anthraquinone by treating the nitramines of anthraquinone with mineral acids.

British Dyes Ltd., are also applying for licence to use a further score of German dye patents, and the Controller of Patents, Mr. Temple Franks, in contemplating this activity of British manufacturers, observed that it was important to bear in mind that the German dye industry had flourished by manufacturers devoting themselves each

to separate and well defined departments of dye manufacture. It would be well if British manufacturers could bring themselves to confer and agree to proscribe the whole field by dividing their forces and each prosecuting their research and manufacture in areas duly delimited. There would be both inevitable waste of energy and over-production, in some directions, if every manufacturer, by ignoring the rest, endeavoured himself to cover the whole field. There might come a time when the Patents Court would have to consider the advisability of refusing licences, except with conditions of this kind. For the present, however, he should advise the Board of Trade to grant all the licences asked for.

CHEMISTRY AND WAR.

UNDER this title the *Norwegian Journal of Chemistry, Pharmacy, and Therapy* (No. 8, 1916) reports a lecture delivered by Mr. H. Goldschmidt to the Norwegian Chemical Society, as follows:—

The direct connection between chemistry and war commenced on August 25, 1346, when Edward III. conquered the French at the battle of Crécy by the aid of guns and gunpowder. From this moment it became the aim of all states to provide themselves with great reserves of sulphur, coal, and saltpetre, which, particularly in the case of the latter, presented considerable difficulties, as only in India, Poland, Hungary, and Russia pure saltpetre strata were to be found.

In earlier times other countries had to rely upon the so-called saltpetre-earth for their supplies. This was produced by the putrefaction of organic nitrogenous substances when together with lime or wood-ash. Elutriation of this with the addition of potash gave saltpetre.

All saltpetre-earth was therefore proclaimed Crown property and the saltpetre manufacturers became of considerable importance. Large plants were established where the putrefied organic matter produced ammonia, which, with the addition of saltpetre-earth with its nitro-bacteria, was oxidised by the oxygen of the air into nitric acid.

The second substance required, potash, also caused considerable difficulty owing to the fact that at that time potash was also used for soap and glass making instead of soda as at present, with the consequence that a shortage of potash frequently occurred.

Frederick the Great writes in his book of the seven years war that he, at its commencement, had a stock of 2800 tons of gunpowder, which was equivalent to 2,000,000 kilos. saltpetre.

Owing to the continually increasing consumption of potash, the French soap manufacturers had commenced using soda which was procured from Spain, and the resulting soap was the world famous Marseilles soap. This, however, was of no avail, as the consumption of potash was still too great for the production of saltpetre. During the French revolution, where gunpowder was not spared, demand was made in 1794 for a cheap and practical method of making soda. This was answered by the famous Leblanc, who had a soda factory using sodium chloride as a raw material.

This discovery turned conditions topsy turvy. The price of soda was reduced to a minimum, which also had its influence on soap and glass manufacture.

Thus, war was the direct cause of this great chemico-technical advance. The next occasion upon which something similar occurred was when the manufacture of beet-sugar had its birth under the Napoleonic wars. The sugar contents of beet was discovered by Markgraff in 1747, and in 1786 Achard commenced operations on an industrial scale in the neighbourhood of Berlin. The King of Prussia granted him a loan of 50,000 thaler, and the first sugar factory in Künern was built. As the war stopped the importation of cane-sugar so this method of manufacture increased and spread to other countries, and although the method died down to a great extent after Napoleon's

fall, it has—after the introduction of improvements in the cultivation of beet and manufacture—now to a great extent supplanted cane-sugar.

War has shown its awakening influence upon chemistry, but chemistry has later revolutionised war. The discovery of mercury fulminate altered the old flint lock to ignition by percussion caps and nitroglycerin and guncotton has given us smokeless powder, &c.

In the present war, where the central powers have been almost cut off from the world, chemical discovery has scored great triumphs and, to a considerable extent, contributed to their ability to defy a world of enemies for so surprisingly long a period. At the commencement of hostilities the first problem tackled was to secure an uninterrupted supply of such chemicals as were essential for carrying on the war.

Nitric acid was produced from the air by an adaptation of the Birkeland-Eydes method; but as there was not the necessary water power for the whole of the process one had as a rule to be satisfied with oxidising ammonia. The ammonia was procured from the gasworks and coke-producing plants, which are extensive in Germany. In this manner 531,000 tons of ammonium sulphate were produced in 1913, a quantity equivalent to 111,000 tons of nitrogen. But during the same year 774,318 tons of chili saltpetre (sodium nitrate), equalling 124,000 tons of nitrogen, were imported. As, however, the importation of this latter substance is stopped and the consumption of nitrogen has increased rather than decreased, as both the army and the land have to be supplied, all coal is turned into coke before being used. Still this is not enough, and ammonia is produced artificially according to Frank Caro's method, whereby the nitrogen of the air is linked to carbide as calcium cyanamide, which in itself is an excellent fertiliser, but from which can be produced ammonia by the action of water thereon.

The Germans have also another method of producing ammonia, namely, through Haber's method of letting nitrogen and hydrogen act directly upon each other under pressure at a temperature of 500° in the presence of uranium, iron, or other substances which act as catalysts. This is one of the greatest triumphs of chemical science. During 1913 140,000 tons of ammonium sulphate were produced in this manner, equalling 43,000 tons of nitrogen. During the war this method of manufacture has increased to such an extent that the owner of the patent prophesies that Germany in a few years time will be able to produce all their own requirements in the nature of nitrogen and thus be independent of imports. While the question of ammonia was under consideration, Privy Councillor Hempel, of Dresden, suggested that all urine should be collected, as this would produce ammonia after putrefying. The value of the urine thus collected would be considerable, inasmuch as Germany's 70 million inhabitants (reckoned at 1 litre urine per day) would produce ammonia to the value of 273 million marks per annum.

The fact that this suggestion has not been carried into effect proves that Germany's requirements of ammonia have been met in other ways.

By the use of platinum or oxide of iron as catalysts the ammonia is changed, by the aid of the oxygen in the air, into nitric acid.

Besides nitric acid, sulphuric acid is of course of considerable importance in the production of explosives and in industrial affairs as a whole. Neither in Germany nor Austria is pyrites to be found, although zinc-blende may produce some sulphur. The Stassfurter layers have, however, unlimited quantities of sulphates, which are reduced to sulphides and afterwards treated in the same manner as pyrites.

For the production of explosive glycerin and cellulose are also required. Glycerin is still a weak spot in Germany's independence. Various experiments in the direction of converting carbohydrates into fat have not given any final result, and all glycerin has therefore had to be commandeered. The use of cotton for producing gun-

cotton has long since been abandoned, cellulose now being used, which is produced from wood pulp, of which the central powers have plenty.

The use of gun-cotton as a smokeless powder demands a gelatinising fluid, and for this spirit ether and acetone have been used. The spirit is distilled from potatoes, Germany's national plant. Ether is produced from the spirit and acetone is got from acetic acid, which again comes from the dry distillation of wood or by the yeasting of sugar with bacillus macerans, whereby alcohol and 30 per cent acetone is produced. Picric acid, T.N.T., &c., which are indispensable in the manufacture of explosives, are produced from coal-tar, the treatment of which has of course been carried further in Germany than anywhere else in the world.

Germany's coal-tar industry had prior to the war reached such dimensions that coal-tar had to be imported to get a sufficient supply of raw materials. This import is no longer possible; but as all Germany's coal, as before mentioned, is now turned into coke, the loss is thereby balanced.

The use of chlorates and perchlorates is also large in the making of explosives, and these are produced electrolytically from Stassfurter potassium chloride and sodium chloride. Altogether these rich deposits of potassic salts have given the central powers a leading position in supplying the world. Thus the discontinuation of export has caused shortage in most countries. By the electrolyses of these alkaline chlorides hydrogen, alkali, and chloride are collected. Hydrogen is used for the Zeppelins, while the chlorides are used for the gas-shells. The so-called lachrymatory shells in another way, which is secret. Germany's ability in the direction of producing modern war material seems thus almost unlimited; but at the same time that country's usefulness as regards the more beneficial industries is so dominating and powerful that the sudden stoppage of communication with the European states has shaken the earth to its foundation, and everything, supply, demand, transport, prices, &c., are all out of joint. Germany's coal-tar industry has gradually developed to an impressive extent. Of colour substances alone 922 kinds are made, and coal-tar was made useful in many other ways. For instance, benzol—which, mixed with spirit, is used as motor fuel owing to the shortage of benzine. Other products are used as lubricating oils, &c., and the main part of the more recent introductions into the world of medicine come from the same source.

In the colour industry three names stand out pre-eminently: Bayer, who discovered the chemical composition of indigo and introduced its first synthetics; Heuman, who solved the technical difficulties in its production; and Krietch, who was its pioneer in the commercial world.

Camphor is indispensable in the production of celluloid and certain explosives, but the war has put a stop to its importation from Japan to Germany. Synthetic camphor is, therefore, made from oil of turpentine. The rubber shortage is eased by various methods of re-making old used rubber, and rubber is also produced artificially. Having found that by the dry distillation of rubber the coal-hydrogen Isoprene (C_5H_8) is obtained, it is therefore possible to work backwards from the isoprene and obtain rubber. The object, therefore, is to obtain isoprene, which is made by the heating of various turps, for instance, oil of turpentine. As the supply of turps is insufficient, experiments have been made with different hydrogens, and it was found that butane (C_4H_{10}) and methyl butane (C_6H_{10}) might be used as bases. Innumerable patents have been registered for the production of such hydrogens from acetylene, acetone, derivatives of alcohol, and the by-products from the refining of paraffin, benzol, phenol, &c. Many of these patents are remarkable for their ingenuity, and it is an acknowledged fact that rubber is now being manufactured.

The subject of artificial foodstuffs has been tackled with feverish energy to alleviate the fearful consequences of the

blockade. We have already mentioned the production of fats from carbohydrates, and from these one also seeks to reach the albumens inasmuch as the carbons of carbohydrates oxygen and hydrogen are sought to be combined with nitrogen from ammonia. Through the works of Emil Fischer on the chemistry of albumens a considerable understanding of its chemical composition has been reached, but as yet no syntheses according to ordinary chemical methods have been found. Whereas through yeast one has reached an indirect method of converting carbohydrates into albumen, inasmuch as the yeast contains a high percentage of albumen, and by nourishing and propagating it with molasses their sugar is converted into albumen.

In the autumn of 1915 Fritz Hayduck delivered a lecture on the manufacture of albumen in quantities by fermenting a thin molasses solution whereto was added phosphoric acid, ammonia, magnesium, and potash salt. Of yeasts one was chosen which does not produce alcohol from sugar but exerts all its energy in propagating itself, inasmuch as it develops twice as rapidly as ordinary yeast.

The yeast produced is good as cattle-food and may also be used for human consumption. The usefulness of the method is therefore dependent upon the country's ability to produce enough molasses—but by-products of other industries may also be used, for instance, starch. Dr. Hayduck expressed the opinion that cellulose could be turned into sugar by the aid of micro-organisms, and made the suggestion that the conversion of cellulose through sugar into albumen would no doubt be made so rapidly that, having read one's evening paper, one would be able to eat it next morning for breakfast.

The deeper reason for Germany's superiority over other countries in chemical matters lies in the close relations between science and industry, invention and manufacture—so that all methods are based upon sound theoretical trials and investigations. This again has its foundation in the army of thoroughly educated and independently working chemists which Germany always has encouraged and continually augments. Justus von Liebig is the father of this laboratory power, and its foundation was laid when he introduced laboratory work into the curriculum of the University of Giessen. Thereby Germany has got well ahead of all other countries and has kept that position.

When Liebig, in 1837, for the first time had visited England he could tell many amusing anecdotes of the theoretical ignorance of English manufacturers, and yet England was at that time industrially supreme. England's shortcomings in the matter of chemical science have been very much disclosed by the world-war rearing asunder the principle of the distribution of work among the various countries.

Prices are the best barometer for showing shortages. For instance, England used annually £2,000,000 worth of aniline dyes, but produced less than 10 per cent thereof. During the war indigo, among other things, has come into its own, whereby its price has gone up from 3s. 3d. to 13s. 6d. per lb. Salicylic acid is six times its normal price, &c.

In America, aniline oil was 10 c. per lb. before the war, and now it is 150 c. Toluol is, in Germany, 450 marks per ton, but in America 12,000 marks. It is, therefore, not surprising to find that the war is costing the Allies far more than it is costing Germany, as their money buys very little, and orders such as "6,000,000 dols. worth of picric acid," which is supposed to have been placed with an Anglo-American company, become possible.

Among the many cases of unknown strength and unknown weakness which the world war has shown us, Germany's enormous power and world importance in chemical science is a serious indication to all nations that a country's strength and wealth consists in the ability and ingenuity wherewith it can develop its natural wealth—for without the will to do this, the country most lavishly treated at the hands of nature will remain helpless and of little use.

REPORT TO THE COUNCILS OF THE CHEMICAL SOCIETY AND THE SOCIETY OF CHEMICAL INDUSTRY. JOINT ABSTRACTS COMMITTEE.

THE representatives nominated respectively by the Council of the Chemical Society and by the Council of the Society of Chemical Industry have given their earnest consideration to the enquiry as to how far it might be possible for the two Societies to co-operate in the production of abstracts.

So far as the general question is concerned, it is the unanimous view of the members of the Joint Committee that, as far as possible, immediate steps should be taken to co-ordinate the activities of the two Societies in regard to the abstracting of chemical literature. It is their belief that not only would such action lead to economies within the range of the abstracts now made, but the way would be opened for a more comprehensive survey of the literature to be abstracted. It is also their conviction that this co-operation between the two Societies would help, in some small degree at least, to consolidate the position of chemical science in this country, and would pave the way for such further developments in this direction as might in course of time be found desirable and practicable. That the present is a favourable moment for the initiation of some such movement can scarcely be denied, since the national significance of industrial chemistry, coupled with and based on the active co-operation of all teaching and research laboratories, has been increasingly realised during the last three years. The Committee is convinced that anything which can help to strengthen the bonds between the different branches of the science would be welcomed by all chemists throughout the country.

It is obvious that any effective form of co-operation must necessitate some changes in the distribution of the material publisher and the development of co-ordinated work in the preparation of the abstracts. So far as the abstracts published by the Chemical Society and by the Society of Chemical Industry are concerned it is agreed that the majority are prepared with a somewhat different objective, and that each Society has maintained a desirable individuality both in the subject matter abstracted and in the method of presentation. Apart, however, from this characteristic of the publications of the Societies there remains an overlap of similar abstracts which present no appreciable differences either in form or substance and appear to be equally suitable for publication by either of the Societies.

As to the extent of this overlap it appears that of the papers which are abstracted for the *Journal of the Chemical Society*, 20–25 per cent are abstracted also from the *Journal of the Society of Chemical Industry*. On the other hand, of the total number of abstracts published in the *Journal of the Society of Chemical Industry*, about 15 per cent (equivalent to about 50 per cent on the non-patent abstracts) are prepared from papers abstracted also for the *Journal of the Chemical Society*.

The Joint Committee, taking these facts into consideration, is of the opinion that the overlap might be avoided by definitely allocating the responsibility for abstracting a particular journal to the editorial staff of either Society. The allocation would naturally be made according to the prevailing type of paper published in the respective journal, and the general result would be that abstracts belonging to the domain of pure chemistry would appear in the *Journal of the Chemical Society*, while those belonging to the domain of applied chemistry would appear in the *Journal of the Society of Chemical Industry*.

The assignment of the overlapping abstracts to one or other of the journals is a matter for detailed consideration, but the Committee is of the opinion that no serious difficulties need be anticipated in this connection, and that the distribution of material can be advantageously adjusted without impairing the value of the respective journals.

It may be said, and said rightly, that under this proposed scheme the members of both Societies would receive somewhat less in return for their annual subscription than has been the case up to the present. The Committee, however, desire to emphasise the fact that, apart from the period of the war, the cost of producing each Journal has steadily risen in recent years, and it is certain that in the near future the question of raising the annual subscription in order to meet the increased cost of rapidly extending publications will have to be faced by both Societies. The Committee would suggest that this difficulty will be met, to some extent at least, by the proposed scheme of co-operation, involving, as it does, a saving in abstractors' fees, in paper, and in printing costs.

The editors estimate that the elimination of the overlap in the two journals would effect a saving of about £200 per annum on the basis of the present membership of the two societies.

The elimination of overlapping material from the two journals renders it desirable to provide facilities for making the abstract publications of the two Societies accessible to the members of both. The Committee believes that many members of each Society would welcome an opportunity of being able to purchase the Abstracts of the other Society, especially in view of the fuller association of scientific and industrial chemistry which has developed so hopefully during the period of the war. Of the total membership of the two Societies, amounting to 7000 (Chemical Society 3000, Society of Chemical Industry 4000), only 1000 are members of both, so that there are some 5000 members who might take advantage of the suggested opportunity of purchasing the Abstracts of the Society to which they do not belong. Whilst only a small proportion of them would probably avail themselves initially of such an arrangement, it is considered that the number would gradually increase and that in any case a subscription of 15s. per annum would amply cover the cost of additional printing and postage involved. Any member of either Society would thus be guaranteed, as stated above, but little less literature than he has hitherto received from his own society, without an enhanced subscription, and would be able to supplement it by obtaining the Abstracts of the Society to which he did not belong for a comparatively small additional payment.

The organisation for the carrying out of this proposal need not involve any editorial changes. All that is required for its successful realisation is a closer co-operation between the editors concerned so as to control the allocation of the abstracts and in some respects the distribution of the abstracting.

The Committee is of the opinion that it would materially enhance the value of the co-ordination to publish the abstracts of the two Societies in uniform size and type. A first step in this direction has already been taken by the Society of Chemical Industry in the publication of the first volume of its Annual Reports in uniformity with those of the Chemical Society. Another point to be noted is that the Abstracts of the Chemical Society are paged separately from the Transactions. This is not the case at present with the Journal of the Society of Chemical Industry, but it is considered desirable that this practice should be adopted. It is further suggested that a suitable system of cross-references between the two sets of abstracts should be instituted.

The Joint Committee accordingly submits the following recommendations for the consideration of the Councils of the Chemical Society and of the Society of Chemical Industry:—

1. That the preparation and publication of the Abstracts of the Chemical Society and of the Society of Chemical Industry be co-ordinated so as to minimise overlapping in the material abstracted.

2. That, provided the Councils of the two Societies give their sanction to the general scheme outlined above, the whole matter be referred again to the Joint Committee, with instructions to submit a detailed report under which the scheme may be brought into operation.

CORRESPONDENCE.

RAMSAY MEMORIAL FUND.

To the Editor of the Chemical News.

SIR,—A Committee has been formed with the object of raising a suitable memorial to the late Professor Sir William Ramsay, K.C.B., F.R.S., by collecting a substantial fund to be utilised for the purpose of promoting chemical teaching and research.

The Committee, after prolonged and careful consideration, have resolved to aim at raising a sum of £100,000, and to devote that sum to two principal objects, viz.:—

1. The provision of Ramsay Research Fellowships, tenable wherever the necessary equipment may be found.
2. The establishment of a Ramsay Memorial Laboratory of Engineering Chemistry in connection with University College, London.

We should hesitate to ask for so large a sum of money in such exceptionally difficult times, were it not that the objects specified are objects of real and urgent national importance. The war has demonstrated in a manner previously unrealised the supreme importance of scientific, and in particular chemical, research to the national life, both in the conduct of the war and in the pursuits of industry and manufacture.

The late Sir William Ramsay was himself engaged up to within a comparatively short time of his death in various important problems concerned with the bearing of Chemistry upon the war, and no one realised more completely than he the potentialities of the plans which have since been formulated by this Committee as a Memorial to him.

It is important that the fund should be raised speedily so that the plans for the Laboratory of Engineering Chemistry and the scheme for the award of Fellowships may be prepared before the end of the war, and so that both schemes may begin to operate with as little delay as possible after the return of peace.

Accordingly, we desire, through the columns of your paper, to appeal to friends and admirers of the late Sir William Ramsay, to old students, to all persons who are interested in Chemistry and its application to industry and manufacture, to contribute to this great national and international Memorial to the late Sir William Ramsay, and to send their subscriptions to the Hon. Treasurers of the Ramsay Memorial Fund at University College, London, W.C. 1.—We are, &c.,

H. H. ASQUITH, President.

D. LLOYD GEORGE, GAINFORD, RAYLEIGH, REAY,
ROSEBERY, H. A. L. FISHER, J. J. THOMSON,
Vice-Presidents.

HUGH BELL, Chairman of the Executive Committee.
GLENCONNER, Treasurer.

June 16, 1917.

FLAVINE.

To the Editor of the Chemical News.

SIR,—With reference to the article on "New Flavin Antiseptic," which appeared in your issue of the 8th of June (cxv., 272), I submit that for English commercial purposes it is undesirable that this product should be given the name "Flavine," as Dr. Browning is reported to have proposed, because there are already two well-known articles of commerce, namely—Flavine, the vegetable extract used as a yellow dye, and Flavine, the coal-tar derivative di-amido-benzo-phenone also used as a yellow dye stuff.

Confusion exists already between the two latter substances in connection with railway traffic, and it is undesirable it should be worse confounded by the addition of another substance under the same name.—I am, &c.,

W. GATHORNE YOUNG.

Analyst's Department, G.N.Ry., Doncaster.

THE CHEMICAL NEWS

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TITRATION OF MAGNESIUM.

By F. W. BRUCKMILLER.

THIS paper deals with the titration of magnesium as applied to water analysis. Two methods are available, one consisting in the precipitation of magnesium as magnesium-ammonium phosphate and titration with 0.10 N HCl after filtration; the other in the precipitation as magnesium-ammonium arsenate and titration of the iodine liberated after treating with acid and KI.

Stelba (*Chem. Centr.*, 1866, 728) suggested that magnesium be determined by titrating the precipitate of magnesium-ammonium phosphate with HCl, using methyl orange as indicator, assuming that one mol. of $MgNH_4PO_4$ requires two mols. of acid. Mead (*Journ. Am. Chem. Soc.*, 1899, xxv., 746) speaks of the accuracy of the method, but points out that nothing is gained by using it owing to the tediousness of washing with alcohol. Cohen (*Ibid.*, 1907, xxix., 1464), however, besides mentioning the difficulty of washing, also reports that it is impossible to obtain concordant results.

After working on this method for some time, we overcame the difficulty of washing the precipitate by filtering with aid of suction, using a "Black Ribbon" filter with a protected cone. Concordant results, however, were not always obtained when the precipitate produced by the usual procedure was titrated, i.e., when the precipitation was made directly in the solution from which the calcium had been removed. Since extreme care was taken to remove all the free ammonia, we concluded that the errors came from impurities in the precipitate. The success of the method depends entirely upon the complete precipitation of the magnesium as pure $MgNH_4PO_4$. The conditions for such a precipitation have been pointed out by Gooch and Austin (*Am. J. Sci.*, 1899 [4], vi., 187), and by Neubauer (*Z. Angew. Chem.*, 1896, ix., 839). These are, that the solution be neutral and as free as possible from ammonium salts, and that the ammonia be added after the phosphate solution has been added. The first and last precautions were carefully observed, but no special effort was made to see that the second one was fulfilled.

Now the standard acid added reacts with the PO_4 —— present in the precipitate forming H_2PO_4 —. If some of the magnesium is present as $Mg_3(PO_4)_2$ or as $Mg_2(NH_4)_4(PO_4)_2$ the results in the former case will be too low and in the other too high. The tendency for the formation of the two compounds should be eliminated. The former can be avoided by keeping the solution just alkaline while adding the precipitant, and the latter by avoiding an excess of ammonium salts.

In water analysis all but the latter condition is easily avoided. Ammonium salts do accumulate in the solution and to such an extent as to contaminate the precipitate. These salts must be removed by evaporation and ignition before the titration of magnesium can be made successful. This operation required time, and in ordinary routine work is not always resorted to. If the precipitate is to be titrated, however, this step is necessary. A number of waters were analysed for magnesium by the titration method and by the pyrophosphate method both with and without previous evaporation and ignition, with the results shown in Table I.

In every case where the ammonium salts were not removed too high results were obtained by the titration method. Strict attention must be given to details in obtaining a pure magnesium precipitate if it is to be titrated. Evaporation and expelling of ammonium salts requires

time, and so much so that this one operation defeats the end for which the method was devised, namely a hastening of the magnesium determination. Accurate results can, however, be secured by using it, for, in comparing the two methods by using pure salts concordant results were obtained each time. For reference we give the procedure which we found to give the best results.

TABLE I.—Parts per Million of Magnesium.

Ammonium salts absent.		Ammonium salts present.	
Pyrophosphate.	Titration.	Pyrophosphate.	Titration.
25.00	24.00	26.00	24.90
33.29	30.20	35.60	34.80
40.19	40.26	42.14	43.00
36.76	36.80	40.20	38.40
51.92	51.85	53.64	52.15
60.87	60.80	62.48	63.24
75.86	75.81	77.98	76.74
74.92	74.79	76.83	75.80

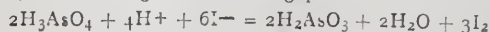
The solution containing magnesium is evaporated to dryness and the ammonium salts are carefully removed by heating. The residue is taken up in a small volume of water, acidified with HCl and, after filtering, made slightly alkaline with ammonium hydroxide. Microcosmic salt solution is slowly added to the cold solution with stirring, and after the precipitate has formed, a volume of ammonium hydroxide equal to one-third of the total volume added, and the solution allowed to stand eighteen hours. The precipitate is filtered off on a "Black Ribbon" filter with the aid of suction and washed with 25 cc. of alcohol. The precipitate is washed with hot water from the filter into the beaker in which the precipitation took place. A known excess of 0.10 N HCl is added, and the excess titrated back with 0.10 N NaOH, using methyl orange as indicator.

The second method applicable to water analysis was suggested by Meade (*Journ. Am. Chem. Soc.*, 1907, xxix., 746) and later revised by Cohen (*Ibid.*, 1907, xxix., 1464). The latter reports favourably on the method provided starch solution is not used in the titration. This method consists in making the concentrated and acid solution decidedly alkaline with ammonia, and precipitating the magnesium with sodium arsenate, agitating the solution while the reagent is being added. After settling, the precipitate is filtered and washed with dilute ammonia solution and then dissolved in hot water. Sulphuric acid is added and, after cooling, KI. The liberated iodine is titrated with thiosulphate without starch.

In using the method in our laboratory, several sources of error not mentioned by the above investigators were found. For the complete precipitation of the magnesium a decided excess of sodium arsenate is required. The excess of arsenate must, however, be at a minimum so as to reduce the wash water to a minimum and thereby avoid solution of the precipitate. An excess of 25 per cent arsenate was the least that could be used if comparable results were to be obtained. This quantity was found to be completely removed by 20—25 cc. of wash water.

The solution in which precipitation takes place should be made decidedly alkaline with ammonia by the addition of 10 cc. of ammonia in excess of that necessary to neutralise the acid and should be free from ammonium salts. Since in water analysis the solution after precipitation of calcium is rich in ammonium salts, it is necessary to evaporate to dryness and remove by ignition, in order to obtain a pure precipitate of $Mg(NH_4)AsO_4$. This requires time and hence this method is open to the same objection as the one previously discussed.

The second great error occurs in the titration of the liberated iodine. Mead suggested the use of thiosulphate after the arsenate had been reduced with KI in acid solution, the following reaction taking place—



This reaction is reversible, the value for the mass law constant being—

$$\frac{(\text{H}_3\text{AsO}_4)_2(\text{H}^+)^4(1^-)}{(\text{H}_3\text{AsO}_3)_2(\text{I}_2)_3} = K$$

In order for the reaction to go to the right the solution must be decidedly acid; that is, the (H^+) must have such a value as to materially increase the oxidising power of the arsenic acid (Stieglitz, "Qualitative Analysis," part i., 283), otherwise the reaction will not go in the desired direction. The volume of the solution during the titration should, therefore, be not greatly increased or else the concentration of H^+ will be so decreased that the reaction will reverse itself. At no time should the volume of the acid (specific gravity 1.16) be less than one-tenth of the volume of the solution.

Again, acidulated solutions of potassium iodide are also very easily oxidised by the air, whereby the concentration of the I_2 is considerably increased. Excessive HCl also liberates iodine and also decomposes thiosulphate. These errors are small and to a large extent neutralise each other. The errors from the other sources mentioned, however, are all positive and lead to higher values than the theoretical. At least, such was our experience even with careful manipulation and strict attention to details so as to avoid such conditions as produce errors. After careful experimentation on various procedures which differed only as to concentrations of reagents used, the following procedure was found to give more nearly theoretical results.

The solution is entirely freed from ammonium salts by evaporation and ignition. The residue is taken up by a small quantity of HCl and filtered. The solution is cooled and an excess of 10 cc. of ammonia added. A 10 to 20 per cent excess of sodium arsenate is added slowly and with vigorous stirring, the stirring being continued for about ten minutes after no further precipitation takes place. The solution is allowed to stand in a cool place to allow the precipitate to settle, and is then filtered and washed with ammonia water (3 per cent). The precipitate is dissolved in hot water and washed into the beaker in which precipitation took place, and 10 cc. HCl (conc.) and 0.3 gm. KI added for every 100 cc. of liquid. The liberated iodine is titrated with 0.10 N thiosulphate. Some typical results are given in Table II.

TABLE II.—Magnesium in Parts per Million.

By titration.	By pyrophosphate.	By titration.	By pyrophosphate.
25.61	26.41	50.73	52.00
25.82	26.38	80.98	81.65
35.40	36.00	80.87	81.92
35.55	36.49	100.50	101.25
50.62	51.23	100.45	101.56

Better results were obtained by using a method suggested by Gooch and Browning (*Am. J. Sci.*, 1890 [3], iii., 40, 66), in which the arsenious acid was titrated with iodine after expelling the liberated iodine in the original solution by boiling with sulphuric acid. One modification, however, was made. Instead of using the sodium bicarbonate as neutralising agent, we made use of sodium phosphate (Washburn, *Journ. Am. Chem. Soc.*, 1908, xxx., 37) along with sodium hydroxide, which procedure more easily permits keeping the H^+ ion concentration of the solution at the proper value than the use of sodium bicarbonate. For every 100 cc. of 0.10 N iodine used, 11 grms. of $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ are necessary in a volume of 250 cc. to keep the ratio $\text{Na}_2\text{HPO}_4/\text{NaH}_2\text{PO}_4 = 2$ at the end point, which insures a concentration for H^+ of 10⁻⁷. This quantity of iodine would be equivalent to 480 mgrms. of magnesium per litre, a quantity rarely found in water. To aid in keeping the ratio at the proper value, we found it convenient to start with a volume of about 100 cc. and at the end of the titration, if added reagents did not make the volume 250 cc., distilled water was added. The phosphate solution was made up so that 50 cc. contained 11 grms. of salt. The volume necessary to add is

then half the volume of 0.10 N iodine used. A few typical results are given in Table III.

TABLE III.—Magnesium in Parts per Million.

By titration.	By pyrophosphate.	By titration.	By pyrophosphate.
25.47	25.51	50.70	50.72
25.90	25.94	75.80	75.90
35.62	35.60	75.87	75.90
35.75	35.72	100.23	100.26
50.61	50.59	100.37	100.35

The procedure used follows:—The solution from the calcium precipitation is evaporated to dryness and the ammonium salts are removed by ignition. The residue is taken up in hot water, acidified with HCl , filtered, and an excess of 10 cc. of ammonium hydroxide added. Sodium arsenate is added in excess, 10 to 20 per cent, and the whole solution cooled and shaken or stirred for ten minutes. The precipitate is allowed to settle in the cold, after which it is filtered and washed in dilute ammonia water (3 per cent). The precipitate is dissolved in hot water, and the solution caught in an Erlenmeyer flask. An excess KI is added and 10 cc. H_2SO_4 (1:1). The whole is boiled rapidly with a trap in the Erlenmeyer flask until iodine vapours are no longer visible. While still hot, the small trace of iodine remaining is destroyed with sulphurous acid and the whole cooled quickly. The acid solution is neutralised with 0.10 N NaOH , using phenolphthalein as the indicator, adding from time to time some of the phosphate solution. When titration is complete, the volume of phosphate solution added should be equal to one-half the volume of the iodine solution. The volume should be about 250 cc., and if greater than this, more phosphate must be added in proportion to keep the concentration of H^+ at the right value. The arsenious acid is titrated as usual, using 0.10 N iodine.

Judging from our experience, the magnesium can be determined volumetrically provided great care is taken in the formation of the phosphate precipitate on the one hand, and on the other that special precautions are taken in the titration of iodine liberated by the arsenate precipitate from potassium iodide or the arsenious acid remaining after all the iodine has been expelled. Detailed procedures have been given which have been found to give results comparable with those by the usual gravimetric procedure.—*Journal of the American Chemical Society*, xxxix., No. 4.

THE CONTROL OF THE LEAD CHAMBER PROCESS IN VITRIOL MANUFACTURE.*

By A. M. FAIRLIE.

It is well known that the largest single item of expense in operating a sulphuric acid chamber plant is nitrate of soda. Efforts to improve the economical operation of such a plant are naturally directed, therefore, towards the conservation or the recovery of the valuable nitrogen compounds. The most important of the inventions designed to effect a saving in the consumption of nitrate of soda was of course the Gay-Lussac tower. Since the use of that tower for the recovery of the oxides of nitrogen escaping from the last chamber has become universal, wherever the chamber process is in operation many devices have been introduced to improve the efficiency of the tower. These include various styles of packing material, various ways of distributing the acid fed on the top, the use of water instead of steam in the chambers, the introduction of towers fed with cold acid between the chambers to effect greater cooling of the chamber gases, and so forth.

Even with the best of these improvements installed, the efficiency of the Gay-Lussac tower will depend largely

* A paper read before the Georgia Section of the American Chemical Society.

upon the way the process is handled—upon the proper regulation of the streams of acid on the towers, and of the steam or water in the chambers; upon the efficient cooling of the acid used on the Gay-Lussacs; upon the avoidance of interruptions due to break-downs; and, above all, upon the careful introduction of the sulphur dioxide admitted to the chambers per unit of time.

Let us assume that the plant has been designed and constructed intelligently—that proper materials of construction have been used; that spare pumping appliances have been provided to permit the uninterrupted flow of the streams of acid over the towers under any possible conditions; that by-pass flues or spare fans have been installed, to insure the continuous and uniform flow of gas, even in case of breakdown; that the plant, in short, has been built under the direction of a competent sulphuric-acid engineer, experienced in operation as well as in construction—let us assume further that the plant is manned by a competent crew of workmen, able to operate the appliances without interruption, and turn our attention to the regulation of the nitre into the system.

The well-known, time-tried methods of regulating the quantity of nitre introduced, or, let us say, of controlling the process, are: (1) by observing the differences between chamber temperatures at different parts of the system, learning by experience what differences yield the best recoveries in the Gay-Lussac tower, and endeavouring thereafter to maintain such desirable temperature differences constant. (2) By observing the colour of the gases in the chambers or connecting pipes by means of windows or "sights." (3) By a combination of both of the above methods.

These methods may be satisfactory in the main, as long as the gas entering the Glover tower contains a substantially uniform percentage of sulphur dioxide, but it is questionable if, even under the best of conditions as regards uniformity of grade of burner gas, these methods are adequate to yield the most economical results. To control by these methods is to control by symptoms, whereas the rational method of control is by analysis of the gases. Certainly when the grade of burner or furnace gas is irregular, as in the case of plants manufacturing acid as a by-product of zinc or copper-smelting operations, the time-tried methods of control should be replaced by the analytical method. The temperature-difference method fails when operating on a fluctuating burner gas, because the indications of the temperature-differences are misleading. The same change in the temperature-difference may be due to one of several causes, and as the temperature-difference does not indicate in case of trouble to which cause the trouble is due the wrong remedy may be applied. The colour method alone is altogether inadequate as a guide for controlling the chamber process. In the first place, the sight glasses are usually placed at the back end of the chamber system, whereby information about the colour of the chamber gases is obtained too late to prevent the damage which has been done; and besides, even if the sight glasses are in the front chamber, the colour there is so obscured by the white mists that few persons possess the ability to detect the differences in shade, by day and by night, which would indicate whether or not the gas mixture contained the correct amount of nitrogen oxides.

The Fairlie method of controlling the chamber process (U.S. Patents, Nos. 1,205,723 and 1,205,724) is the only analytical method known to the industry. It has been in continuous daily use at the plant of the Tennessee Copper Company, where it was invented, for the past six years, and has proved its value every day that it has been in use. It consists in determining the percentage of sulphur dioxide in the chamber gases at some point near the end of the chamber system, and in comparing such percentage with the percentage sulphur dioxide in the burner gas before admixture with nitre fumes. The comparison shows, after experience, that a certain ratio between the two sulphur dioxide percentages must be maintained in order to secure

the best results in the Gay-Lussac tower. What this desirable ratio is must be determined for every possible grade of burner gas. Once determined, the desirable ratios are set down in tabular form on a card, which is framed and fastened in a convenient place for reference by the chamber operator. This operator keeps his analytical apparatus in good order at all times, and by taking frequent gas tests of the burner gas and of the front chamber gas, accurate indications as to the condition of the gas mixture and as to the speed of oxidation of sulphur dioxide are obtained, and obtained in time to apply the proper remedy in case anything is about to go wrong. An increase in the sulphur dioxide ratio above what is desirable indicates the need of more nitre; whereas a decrease below the desirable ratio indicates that the quantity of nitre must be reduced.

The analytical method adopted for determining the sulphur dioxide percentage in the gases is the Reich method—in its original form for the burner gas, but modified by the addition of solution of acetate of soda and acetic acid to the absorption bottle for the chamber gas. The original unmodified Reich method is impossible for the chamber gas, because the presence of nitrogen oxides causes the starch iodide blue colour to recur, and vitiates the results. The Reich method, as modified, will give results on chamber gas agreeing with 0.01 per cent, and this is sufficiently accurate for the most careful control of the process. The method of testing the gases can easily be learned by a workman of usual intelligence, so that the expense of employing a chemist for the analysis of the gases is avoided.

It may be remarked in this connection that by means of the modified Reich method, as applied to chamber gases, important information may be obtained regarding the percentage of sulphur dioxide desirable in the gases entering the Gay-Lussac. Some of our old acid makers—and, indeed, some of our old acid engineers—grown grey in the sulphuric-acid industry, scoff at the idea of any sulphur dioxide being desirable in the Gay-Lussac tower gases. This is because the older men are not familiar with any rapid method for determining accurately the percentage of sulphur dioxide in gas mixtures containing nitrogen oxides. And because the methods of analysis which they used failed to indicate the presence of sulphuric dioxide at the Gay-Lussac tower, they have formed the conclusion that none is ever present, under normal conditions. The facts, however, are these:—

The nitrogen oxides are recovered most completely in the Gay-Lussac tower when the proportion of nitric oxide (NO) and nitrogen peroxide (NO₂) in the gases entering that tower are such that the combination gives nitrogen trioxide (N₂O₃) with no excess of either of the constituent gases. The presence of a small quantity of sulphur dioxide is needed in the gas mixture entering the Gay-Lussac to keep a sufficient amount of the nitrogen gases reduced to the nitric oxide form. If the quantity of sulphur dioxide present be deficient, or if there be none at all, an excess of nitrogen peroxide will be present, above what is needed to combine with nitric oxide to form nitrogen trioxide, and this excess, being only slightly soluble in the cold 60° acid with which the tower is fed, will be lost, as indicated by the red fumes escaping into the air through the exit stacks. On the other hand, if too much sulphur dioxide be present in the gas mixture entering the Gay-Lussac, an excess of nitric acid, above the quantity needed to combine with the nitrogen peroxide to form the trioxide, will be present. As nitric oxide likewise is only slightly soluble in cold sulphuric acid of 60° strength, this excess will be largely lost, as before, although, because the nitric oxide is a colourless gas, the loss will not be so readily detected by observation of the colour of the gases escaping from the top of the tower as in the case of the red gas, nitrogen peroxide. For this reason it is of especial importance to have some other means of knowing when there is an excess of nitric oxide present in the gases entering the Gay-Lussac. By means of the modified Reich test it has been

demonstrated that the right proportions of nitric oxide and nitrogen peroxide will be present when the percentage of sulphur dioxide entering the Gay-Lussac is between 0.07 and 0.10 of 1 per cent in cold weather, or between 0.09 and 0.12 of 1 per cent in moderate or warm weather. Under moderate weather conditions any deviation in the percentage of sulphur dioxide above the high limit of 0.12 per cent indicates an excess of nitric oxide, and any deviation below the low limit of 0.09 per cent indicates an excess of nitrogen peroxide, so that careless handling of the process at the front end of the system will be plainly indicated by testing the gas at the entrance to the Gay-Lussac tower.

The analytical method of controlling the chamber process ought to eradicate that old advice to the chamber operator: "In case of trouble, first increase your nitre at the pots, then find out what is wrong." This advice, advocated by two such authorities as Lunge and Falding, is, on the face of it, absurd. How foolish to add more nitre in case of trouble, when the thing that is wrong may be already too much nitre. The rational thing to do in case of trouble is to proceed by the indications of the analytical method. First find out what is wrong by analysis of the gases (thirty seconds of time is all that is needed), then either increase or reduce the quantity of nitre, according to indications.

The analytical method of controlling the chamber system is particularly valuable in starting up a set of chambers after a shut-down, or in starting up a new plant for the first time. It has been the experience of most chamber-plant owners that in starting up a plant a period of experimentation must elapse, varying from two weeks for an old plant to several months for a new one, before the chambers settle down to regular work. The reason for this is that nobody knows, in starting up a plant, what is wrong, because the time-tried methods are useless while the process is upset. The analytical method of control, on the other hand, indicates precisely what is wrong, and indicates to what extent it is wrong, thus permitting the proper remedy to be applied, in the correct proportions. By means of the analytical method of control the immense plant of the Tennessee Copper Company has been repeatedly put into regular working condition, after a shut-down, within thirty-six hours. The new 400-ton plant of this company, started for the first time last July, and using the analytical method of control was in regular working condition forty-eight hours after the gas was first admitted to the Glover tower.—*Chemical Engineering and the Works Chemist.*

FERROCERIUM AND OTHER PYROPHORIC ALLOYS.

A RECENT issue of the *Engineering and Mining Journal* (1917, [5], p. 212) contains the following notes on pyrophoric alloys:—

About the year 1903 Welsbach discovered that certain alloys of the rare earths, when filed, gave off showers of bright sparks which would readily ignite inflammable gases. It was subsequently found that the best results were secured when employing an alloy containing about 65 per cent iron. The same action takes place with these alloys as with the flint and steel, except that a spark is produced much more easily than with the primitive tinder-box.

The mixture of certain earth metals, often called *misch* metal, consists mainly of the elements cerium, lanthanum, didymium, neodymium, praseodymium, and samarium. All these metals are white to light yellow in colour and not readily oxidised in the air. The commercial *misch* metal varies in character according to the manufacture. For example, the *misch* metal produced by one large German chemical manufacturer is quite soft, whereas that produced by another manufacturer by electric reduction is

quite hard and often very brittle. The brittleness in most cases is caused by the presence of silicon as an impurity. Welsbach patented his discovery and for a time monopolised the market. Subsequently the German courts limited the operation of the patent and at one time threatened to annul it entirely.

The price of ferrocium alloys when first produced was about £12 per kg. Later this was reduced to £2 8s. per kg. and in 1913 to about £1 per kg.

While the original pyrophoric alloy (ferrocium) manufactured by Welsbach contains nearly 40 per cent iron, the competing products have only about 15 per cent iron, and for the purpose of hardening, about 2 per cent antimony or bismuth is added. Silicon is found in nearly all ferrocium alloys, because it is either contained in the raw *misch* metal as an impurity or has been absorbed from the clay crucibles in which the alloy is often produced. To produce a low-melting and smooth-casting pyrophoric alloy, certain manufacturers add about 5 per cent copper. Various theories have been advanced to explain the pyrophoric character of ferrocium alloys, and various authorities claim that it is due to nitrides, hydrides, or sub-oxides. None of these theories have been substantiated, however.

Several alloys, interesting solely from a scientific standpoint, have been produced with mercury and platinum. The former is highly explosive. The latter alloy, when containing about 25 per cent platinum, possesses the greatest pyrophoric properties of any of the known cerium alloys. A zinc-cerium alloy is especially suitable for the ignition of mine lamps. Cerium alloys containing boron have also been recommended for a like purpose.

By the addition of 25 per cent aluminium or magnesium to the cerium alloys, a very brittle metal is produced, which is readily pulverised. Inferior pyrophoric alloys containing high percentages of carbides are very unstable, and unless protected from the air by a film of oil, readily oxidise and become worthless within a few weeks.

The raw material for the manufacture of ferrocium is generally the waste from gas mantle factories, which consume large quantities of monazite sand. After the extraction of the thorium from the sand, there is produced as a by-product what is known as rare earth residues or *misch* metal oxides. Most manufacturers produce ferrocium by the electrolysis of the anhydrous chlorides of cerium, lanthanum, didymium, &c. A good grade of mixed anhydrous chlorides costs, under normal conditions, about 3s. per kg. The fluorides of the cerium metals have not proved satisfactory, as they produce a thick, pasty metal in which the *misch* metal separates in a fine state of distribution and not in the form of a solid mass as in the case of the chlorides. For the production of ferrocium by the electrolytic process, it is necessary that cheap current be available. Many manufacturers use ordinary graphite or clay crucibles with large iron cathodes. Others use water-jacketed iron crucibles.

In the early days of the industry, the small pocket lighters, in which the pyrophoric alloy was employed, contained only small pieces of metal weighing from $\frac{1}{4}$ to $\frac{1}{2}$ gm., and these lighters were regarded more or less as scientific toys. At the present time there are two distinct types of lighters on the market, in one of which the pyrophoric alloy is fed in the form of a small stick against a hard steel wheel with a file-like surface; this wheel, when revolved, produces a shower of sparks, which are projected on a cotton wick impregnated with benzine or gasoline. The other type or lighter consists of a long strip of pyrophoric alloy against which a hard steel pin is struck; around this is wrapped an asbestos thread, which is kept saturated, when not in use, with gasoline in a small reservoir constructed in the body of the lighter.

The largest consumption of ferrocium in the United States is for patent gas-lighters. In Europe, where the match industry is a government monopoly, the main consumption of ferrocium is for cigar lighters.—Extract from the *Journal of the Society of Chemical Industry.*

FIFTY GERMAN DYE INVENTIONS.

BRITISH DYES, LTD., AND THE POST-WAR RANGE OF SPECIFICATIONS.

(From a Correspondent).

BRITISH DYES, LTD., have now been to the Patents Court for fifty German dye inventions, including the most modern, of which notification has been received in this country only since the war broke out, and it is stated that there is a further range of specifications for which they mean to apply.

A score of these patents were set out in the *CHEMICAL NEWS* (cxv., 272). On Thursday, June 7, British Dyes, Ltd., again attended at the Court and asked the Controller (Mr. Temple Franks) to licence to them the use of two further German patents, including that for Flavine, and thirty "unsealed patents," which are specifications sent to this country to be sealed as patents here, and "hung up" because of the outbreak of the war. The practice is to vest these in the Public Trustee as custodian, and he issues a licence for their use on payment of the usual fees.

The post-war inventions, with the name of the owners heading each group, are as follows:—

Badische Anilin und Soda Fabrik.

23541 of 1913 (product, sulphuric acid)—The use of vanadic acid for the conversion of SO_2 into SO_3 .

17,764 of 1914—Manufacture of anthraquinone dyes by treating 4-amino-1-aryldio-anthraquinone-3-sulpho-2-carboxylic acid with a condensing agent.

20,615 of 1914 (intermediate)—Manufacture of diamino-diaryl-ketones and diamino-diaryl-thio-ketones by treating diamino-diaryl-methanes with polysulphides.

3347 of 1915—Manufacture of β -aryldio-anthraquinones by heating anthraquinone-2-sulphonic acid with an aryl-amino compound in the presence of caustic alkali.

8058 of 1915 (intermediate for azo-dyes)—Manufacture of halogenated benzoyl derivatives of 1-amino-7-naphthol by causing halogenated benzoyl chloride to react on 1-amino-7-naphthol.

100,581—Manufacture of aryl derivatives of anthraquinone from anthraquinone-2-sulphonic acid and a suitable arylamino compound.

100,580—Manufacture of β -anilino-anthraquinones by heating anthraquinone-2-sulpho acid with aniline in the presence of caustic alkali.

Friedrich Bayer and Co.

15,165 of 1913 (product, sulphuric acid)—Use of asbestos impregnated with silver vanadate as contact material.

13,866 of 1914 (medical product)—Manufacture of ureas of the naphthalene series by treating with phosgene such 1:8 amino-naphthol sulphonic acids as are substituted in the amino group by the aminobenzoyl residue.

17,743 of 1914—Manufacture of blue lake colours by converting into aluminium lakes the sulphonic acids of quinizarine.

17,744 of 1914—Manufacture of violet-blue lake colours by converting into aluminium lakes the sulphonic acids of 1-amino-4-oxyanthraquinone.

13,952 of 1915—Manufacture of blue sulphur colours by treating indophenols or leuco-indophenols with alkali polysulphides.

Meister, Lucius, and Bruning.

4540 of 1915—Manufacture of anthraquinone dyestuffs by treating trihalogen- α -amino-anthraquinones with an aromatic amine.

8489 of 1915—Manufacture of yellow azo-dyes by combining a diazotised ester of 4-nitro-2-aminobenzoic acid with β -naphthol.

Actien-Gesellschaft für Anilin Fabrikation.

4072 of 1915—Manufacture of disazo-dyestuffs by combining 4,4'-diaminodi-phenyl-urea with 2-amino-8-naphthol-6 sulphonic acid and resorcin.

5183 of 1915—Manufacture of monoazo dyestuffs for wool by combining 6-acetyl-amino-3-diazo-1-methoxy-benzene-4-sulphonic acid with 2-amino-8-naphthol-6-sulphonic acid in acetic acid solution.

7861 of 1915—Manufacture of greenish-blue anthraquinone dyes by heating 1-amino-4-halogen-anthraquinone-2-sulphonic acid with aromatic amines and water.

7877 of 1915—Manufacture of greenish blue anthraquinone dyes by heating 1-amino-halogen-anthraquinone-6- or 7-sulphonic acid with aromatic amines and water.

8109 of 1915 (intermediate for anthraquinone dyes)—Manufacture of arylsulphaminoanthraquinonesulphonic and carboxylic acids by heating halogen anthraquinone-sulphonic and carboxylic acids with arylsulphamides in aqueous alkaline solution.

8996 of 1915—Manufacture of green substantive trisazo-dyestuffs by combining diazo-naphthalene sulphonic acid with an amino compound of the benzene or naphthalene series and subsequently introducing several other components.

14,789 of 1915—Manufacture of blue tetrakisazo dyestuffs by combining diazotised 2-naphthylamine-4:8-disulphonic acid with 3-tulidine or paraxylidene and several other components.

100,078—Manufacture of yellow azo-dyestuffs by combining tetrazotised 4,4'-diamino-diphenylsulphide-2,2'-disulphonic acid with an aceto-acetarylamine.

Chemische Fabrik Griesheim-Elektron.

610 of 1915—Manufacture of anthraquinone dyes by condensing orthoaminoazo-dyestuffs with anthraquinone-2-aldehyde.

5444 of 1915 (intermediate for chroming dyestuffs, &c.)—Manufacture of the arylides of oxyaryl-carboxylic acids by treating these acids with aminoaryl-carboxylic acids in the presence of a dehydrating agent.

5445 of 1915 (intermediate for azo dyestuffs)—Manufacture of oxynaphthoyl derivatives of amino-naphthol-sulphonic acids by causing halogenides of 2:3 oxy-naphthoic acid to react with amino-naphthol-sulphonic acids.

5446 of 1915 (intermediate for azo dyestuffs)—Manufacture of oxynaphthoyl derivatives of aminonaphthols by condensing o-acyl derivatives of 2:3-oxynaphthoic acid with amino-naphthols and saponifying.

6663 of 1915 (preparation for azo dyestuffs)—Manufacture of preparations consisting of concentrated mixtures of alkali salts of nitrosamines and alkali salts of the aryl-amides of 2:3-oxynaphthoic acid.

8254 of 1915—Manufacture of mercaptans of the anthraquinone series by treating α -oxy- and α -amino derivatives of anthraquinone with alkali-sulphide.

14,103 of 1915—Manufacture of anthracene dyes by treating an alkali salt of pyrazole-anthrone-yellow with material for introducing an alkyl or an aralkyl group.

Casella and Co.

17,319 of 1914—Manufacture of dyestuffs by heating 1-amino-2-methylanthraquinone with sulphur and an aromatic amine.

13,970 of 1915—Manufacture of tetrachloro-benzal-chloride and conversion of same into a triphenylmethane dyestuff by condensation with an o-oxy-carboxylic acid of the benzene series.

24,652 of 1910 (flavine)—Manufacture of 3:6 diamino-acridine by heating a solution of tetramino diphenylmethane in mineral acids in the presence of tin salts.

The Controller enquired of Mr. J. Turner, the managing director of British Dyes, Ltd., whether he proposed to manufacture flavine as a dyestuff or an antiseptic.

He replied—Both. As an antiseptic it must be made chemically pure. As a dyestuff it was a less specialised preparation.

Some of these colouring matters undoubtedly served well as antiseptics. The doctors of the Bland-Sutton Institute had lately demonstrated the pre-eminent value of flavine in war surgery, but there were other dyes which

were similarly used—brilliant green, for instance. Brilliant green, upon which Dr. Ligat, the assistant surgeon at the Middlesex Hospital, had lately reported favourably, had been employed for years as a dyestuff. As an antiseptic, of course, it was sent up as pure as it could be obtained.

Mr. Carpmael, who watched the proceedings for Casella's, observed that two medical products were included in the list of inventions which British Dyes now desired to use—flavine and 13,866 of 1914. Would it be made a penal offence for anybody to use as an antiseptic a product which he had bought as a dyestuff?

The Controller replied that the Food and Drugs Act, or some other act, would doubtless be found to apply. He was troubled at present by the name. It would not do to supply flavine by the same name both as an antiseptic and a dyestuff.

Mr. Turner pointed out that there was the further complication that a vegetable dye was already on the market under the name flavine.

The vegetable dye is a preparation of quercitron bark. The two bodies, however, are chemically related, both being pyrone derivatives.

The Controller said he had now heard five or six applications for licence to manufacture flavine, and obviously there must be some uniformity in the name of the product as it came from all these manufacturers. The Court had fixed the name as Acrid flavine, and it would be necessary for British Dyes to communicate with the Board of Trade as to the name under which they proposed to sell flavine as a dye. It was essential to invent a further name and the Board of Trade would have to approve it. For the rest, he saw no reason against granting the licences now asked for, and they would be issued on the terms of a 2½ per cent royalty on the selling price and 1 per cent on the manufacturers' use of intermediates.

THE "VAN'T HOFF FUND."

IN agreement with the regulations of the "Van't Hoff Fund," founded on June 28, 1913, persons interested are informed herewith of the following particulars:—

The foundation, whose residence is Amsterdam, and of which the supervision is vested in the Royal Academy of Sciences there, is appropriated to give from the rents of the fund every year before March 1 endowments to investigators in the field of pure and applied chemistry, who will have applied for such an endowment before November 1 preceding the above mentioned date, to the Committee charged with considering the applications and awarding the grants.

At present this Committee is constituted as follows:—A. F. Holleman, President; S. Hoogewerff; A. Smits; E. H. Büchner, Secretary. If desirable, this Committee may appoint still other members for one year only, to co-operate in judging of the applications made.

The names of persons to whom a grant is allowed will be published. The grantees are requested to send to the Committee some copies of the papers relating to the results of their work, but for the rest they are at liberty to choose the manner of publication, as well as the journal, in which they like to publish their results if only they mention the fact that the research was made with an endowment from the "van't Hoff Fund."

The amount available over 1918 is about £150.

Applications should be sent, registered by post, to:—*Het bestuur der Koninklijke Akademie van Wetenschappen; bestemd voor de Commissie van het "van't Hoff-fonds," Trippenhuis, Kloveniersburgwal, te Amsterdam*, with a detailed account of the proposed use of the grant, and of the reasons on which the candidates ground their claim. They must be received before November 1, 1917.

In the name of the Committee of the "van't Hoff Fund"—

A. F. HOLLEMAN, President.
Amsterdam, May, 1917. E. H. BÜCHNER, Secretary.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, June 14, 1917.

Sir J. J. THOMSON, O.M., President, in the Chair.

PAPERS were read as follows:—

"Some Cases of Wave-motion due to a Submerged Obstacle." By Prof. T. H. HAVELOCK, F.R.S.

In this paper Prof. Lamb's solution for a submerged circular cylinder is carried a stage further in the approximation, and the wave resistance is calculated directly from the resultant fluid pressure on the cylinder. Similar methods are then applied to a three-dimensional problem, the waves produced by a submerged sphere. The wave resistance is found in the form cons. $\times a^{3/2} e^{-a/2} W_{1,1}(a)$, where a is $2gf/c^2$ with f the depth of the sphere, and c its velocity; $W_{1,1}$ is a confluent hypergeometric function. The law of variation of wave resistance with speed is shown by a graph calculated from this expression.

"Propagation of Sound in the Free Atmosphere and the Acoustic Efficiency of Fog Signal Machinery." By Prof. L. V. KING.

"Behaviour of Scattering Media in Fully Diffused Light." By H. J. SHANNON, F. F. RENWICK, and B. V. STORR.

The paper deals with the relationships between the rejectance, R (proportion of incident light rejected), the obstruction Ω (ratio of incident light to transmitted light), light capacity C (ratio of accepted light $(1-R)$ to transmitted light) when a sheet of diffusing medium is illuminated on one side by diffuse light, and also the relative obstruction, O , the relative density, $D (= \log_{10} O)$, when, as in various instruments, the source of light is a first sheet of diffusing medium in contact with the sheet being examined.

Expressions are deduced for R_{m+n} , Ω_{m+n} , C_{m+n} , and O_{m+n} , of which only Ω_{m+n} is symmetrical with respect to m and n . From these it is shown that the variation with thickness is the same for Ω , C , and O , since $\Omega_{n+2} + \Omega_n = k\Omega_{n+1}$, with similar expressions for C and O ; this leads to the general equation—

$$\Omega_t = P e^{\lambda t} + Q e^{-\lambda t},$$

where—

$$P = \frac{\Omega_1 - e^{-\lambda}}{2 \sinh \lambda}, \quad Q = \frac{e^{\lambda} - \Omega_1}{2 \sinh \lambda},$$

and—

$$k = (1 + R_1)C_1 + \frac{1 - R_1}{C_1} = 2 \cosh \lambda.$$

This equation may be written in various way of which—

$$\Omega_t = \frac{\Omega_1 \sinh \lambda t - \sinh \lambda(t-1)}{\sinh \lambda}$$

is preferred for numerical calculations.

The expression for R_t is similar but more complicated;

$$R_t = \frac{R_1 \Omega_1 (e^{\lambda} - e^{-\lambda t})}{(\Omega_1 - e^{-\lambda})e^{\lambda t} + (e^{\lambda} - \Omega_1)e^{\lambda t - 1}},$$

which becomes by putting—

$$e^{\beta} = \frac{C_1 - e^{-\lambda}}{e^{\lambda} - C_1}, \quad R_t = \frac{\sinh \lambda t}{\sinh (\lambda t + \beta)};$$

putting $t =$

$$R_{\infty} = \frac{R_1 \Omega_1}{\Omega_1 - e^{-\lambda}}.$$

The experimental part of the paper discusses the method of using the theoretical equations obtained for determining the constants of a specimen of diffusing medium, certain requirements of the instrument used, and precautions to be taken. Examples are given showing

the close agreement between observed and calculated values up to seven thicknesses of opal for both air and oil contact.

"Theory of Decay in Radio-active Luminous Compounds." By J. W. T. WALSH.

The theory of destruction of "active centres" put forward by Rutherford (*Roy. Soc. Proc.*, A, 1910, lxxiii., 561) to account for the decay of luminosity of radio-active luminous compounds, leads to a simple exponential relation in the special case of a compound of constant activity.

It has been found for radium zinc sulphide compounds (Paterson, Walsh, and Higgins, "An Investigation of Radium Luminous Compounds") that this relation expresses the observed results to a sufficient accuracy over short periods of less than 200 days, but that it fails to do so over longer periods such as 500 days, the rate of decay of luminosity becoming gradually slower and slower so that the brightness tends to a limiting value which is not zero.

The paper is an attempt to find a luminosity time relation which will allow of the prediction of the ultimate behaviour of compounds of varying composition, and it assumes the operation of some factor acting in a direction opposite to that of the destruction of the active centres.

Such a factor would be the recovery of the destroyed "active centres" at a rate proportional to their concentration in the material, and it is shown that an assumption of this nature represents the observed results to the accuracy of the experiments.

Two applications of the "recovery" theory are given:—(1) The investigation of the ultimate luminosities of compounds containing different proportions of radium in samples of zinc sulphide of the same characteristics. This is of importance in considering the most suitable radium content to employ for any specific purpose. (2) The calculation of the total light emitted by a sample of radium luminous compound during any portion of its life.

An appendix deals with the results to be expected (on the theory of "recovery") from samples of mesothorium luminous compounds in which the age of the mesothorium may be from six months to two years.

PHYSICAL SOCIETY.

Ordinary Meeting, June 8, 1917.

Prof. C. V. BOYS, F.R.S., President, in the Chair.

A PAPER entitled "An Alternating Current Bridge Method of Comparing Two Fixed Inductances at Commercial Frequencies," by T. PARNELL, M.A., was read by Dr. SUMPNER.

The paper describes a method of avoiding the troublesome double adjustment required in Maxwell's method of comparing inductances. A current detector, whose deflections depend on the component of the current in quadrature with the E.M.F., is employed, which makes it possible to arrange that the condition for no deflection depends chiefly either on the inductances or resistances. In series with the bridge is placed either a non-inductive resistance or a capacity. In the first case the balance depends chiefly on the inductances, and in the second case on the resistances. A few alternate repetitions of the two adjustments suffice to balance the bridge, both for resistances and inductances. As detector a sensitive moving coil galvanometer in conjunction with a commutator, or a Sumpner electro-dynamometer, may be employed; the latter proved more satisfactory.

DISCUSSION.

Dr. D. OWEN said that this was simply the Maxwell bridge; but the author had shown how to use it under the best conditions. It was impossible to get satisfactory results without the double adjustment for inductance and

resistance. Mr. Parnell had shown how this could be most easily done by using currents in quadrature with one another for the two adjustments. The difficulty still remained, however, that one adjustment upset the other; but it was satisfactory to note that the desired end was reached in a short time. The method was probably easy to apply with small inductances; but he would expect practical difficulties to arise with large ones. It was difficult to know what the phases of the bridge currents were with respect to the field current of the electro-dynamometer, and there might be some trouble in getting on the right track. A similar method of using the electro-dynamometer had been tried at the Bureau of Standards, a phase shifter being used to turn the phase of the voltage on the field coils through 90° to get balances for the two conditions.

Mr. T. SMITH pointed out that in double adjustments of this nature, if the wrong adjustment were made first, the successive errors got larger instead of smaller. It would have been helpful if the author had extended his mathematics somewhat, and given some criterion (e.g., some function of the various quantities involved being either positive or negative) as to which of the adjustments—inductance or resistance—should be made first.

Dr. BRYAN asked if the method could be used for small inductances of a few micro-henries?

Prof. BOYS asked if inductances with iron cores could be measured, or only air cored coils, in which the sine law was nearly fulfilled?

Dr. SUMPNER said, in reply, that the author had not gone in great detail into the range of usefulness of the method. He might point out, however, that the sine law was not essential to work with the electro-dynamometer. The author did not appear to have experienced any difficulty about the order of the adjustments; though in some cases this might doubtless cause considerable trouble. He admitted the validity of the author's criticism of the paper by himself and Phillips; and agreed that the double adjustment was essential. At that time, however, he was principally concerned with describing the instrument, and was not using small inductances in which the resistance effect was important.

Mr. A. CAMPBELL communicated the following:—Mr. Parnell's system is interesting, and may be of value in other methods where two adjustments are necessary to obtain a balance. In connection with his commutator method it may be mentioned that L. T. Robinson applied a commutator in the galvanometer circuit in a somewhat similar way for testing transformers by inductance methods (*Trans. Amer. Inst. Elect. Engineers*, June 30, 1909, xxviii., 1040).

A Paper, entitled "On the Wave-lengths and Radiation of Loaded Antennæ," was read by Mr. BALTH. VAN DER POL, Jun.

The paper consists of a mathematical treatment of the subject, the following being some of the conclusions arrived at: The radiation resistance of a loaded antenna, and also the radiation from the antenna, are dependent not only on the wave-length, but on the current values at the top and bottom. The radiation cannot, therefore, be

written $\Sigma = \frac{AT^{2/2}}{\lambda^2}$ where A is constant and T is the R.M.S.

current at the base, as is done in most textbooks. Rüdenberg's formula for flat-top or umbrella antennæ is valid only for very long wave-lengths, with a capacity at the top of the antenna very large compared with that of the vertical part, and Austin's table of radiation resistances up to ratios of $l/\lambda = 0.4$ is based on an unjustifiable extrapolation of Rüdenberg's results.

The paper also treats of the directions in which the energy is most strongly radiated under different conditions.

DISCUSSION.

Prof. J. A. FLEMING communicated the following remarks:—The paper seems to me to be valuable and the analysis correct. The formula for the radiation resistance

of a flat-topped antenna, which is commonly called Rùdenberg's formula, has no claim to be attributed to him; it can be at once derived from Hertz's expressions for the forces due to a small oscillator. As I have shown in my book on the "Principles of Electric Wave Telegraphy," third edition, Hertz's reduced expressions are obtained on the conditions that the current has the same value at all points in the rod of the dumb-bell oscillator; and hence applies also to the reduced formula for radiation resistance. The polar radiation curves which the author has delineated for the higher harmonics of the loaded antenna seem consistent with the delineation of the field of electric force round a rod oscillator given by F. Hack from the equations of Abraham (see "Principles of Electric Wave Telegraphy," plate vi., chapter v.). The possibility of projecting upwards in an inclined direction what is virtually a beam of electric radiation is interesting. By observing where the beam comes to earth it may be possible to determine the height of the reflecting masses of ionised air. There is, however, a certain difficulty in exciting any required high harmonic in an antenna, especially if the capacity and inductance are chiefly located at certain points. When the possibility of experimental work returns it will be interesting to attempt to confirm these results experimentally.

A Demonstration of a Method of Preventing Sparking at a Rapid Make and Break, which incidentally produces Colloidal Platinum, was given by Dr. A. GRIFFITHS.

The apparatus exhibited was one described by him in the *Philosophical Magazine* for March, 1895, p. 232. The device consists of a series of electrolytic cells placed as a shunt across the spark-gap.

The electrodes consist of platinum and the electrolyte of strong sulphuric acid. The cells polarise, and on making the gap an E.M.F. is introduced opposed to the E.M.F. of the battery, so that the current rapidly diminishes, decomposing the liquid and doing chemical work.

Dr. Griffiths made the following statements—

1. The platinum cathodes disintegrate and a colloidal solution of platinum is formed.
2. The cathode on the negative side of the spark-gap generally disintegrates to the greatest extent; the next cathode disintegrates less, and so on, the least disintegration occurring in the cell at the positive side of the spark-gap.
3. The cathodes develop, to the naked eye, an appearance as if they were covered with platinum black. Certain plates examined under the microscope seemed covered with numerous craters.
4. The production of gas does not appear to be the same in each of the electrolytic cells in series; sometimes no gas at all appears to be evolved from the most negative cathode.
5. The rate of disintegration of a cathode appears to be small when the cathode is first placed in the sulphuric acid, and appears to increase to a maximum in course of time.
6. One specimen of platinum appears to behave differently from another.

Dr. Griffiths added that by using electrodes made of gold leaf floated on glass with the aid of methylated spirits, he had obtained what was probably colloidal gold. Prof. Hicks, of Sheffield, had told him that he had used electrolytic cells to stop sparking at a pendulum-mercury intermittent contact. He had not observed disintegration of the platinum as far as he (Dr. Griffiths) was aware.

DISCUSSION.

Dr. S. R. WILLOWS said he was interested in the chemical aspect of the experiment. There was no doubt that Dr. Griffiths was the first to obtain colloidal platinum, though he did not call it by that name when the result was originally described. The difference in intensity of the action in different parts of the circuit reminded him of the similar phenomenon which occurs in a train of X-ray valves, in which most of the action takes place in one

valve of the train. Measurements of the potential across each cell would be instructive.

Prof. BOYS mentioned that he had used electrolytic cells to quench the sparking of a pendulum contact in his gravitation experiments. He had not noticed any action on the platinum. To what did Dr. Griffiths attribute the effect?

Mr. A. CAMPBELL communicated the following remarks: Many years ago Helmholtz introduced the use of a condenser, shunted by a suitable resistance, across the spark-gap for the purpose of suppressing the spark. More recently a better system was employed by the engineers of the G.P.O., who kindly communicated it to the National Physical Laboratory, where it has been used with the greatest success on all kinds of spark-gaps (from one break per second up to 1000 per second). This consisted in putting the resistance in series with the condenser. By adjusting the value of the resistance to suit the particular circuit it is nearly always possible to suppress the spark. There is no leak across the break, as in the shunt system.

Dr. GRIFFITHS, in reply to Prof. Boys, said that he thought the disintegration was due to the inductive rush of the current, but many points required investigation.

BRITISH EMPIRE PRODUCERS' ORGANISATION.

Annual Meeting, May 18, 1917.

SIR JOHN D. REES, K.C.I.E., M.P.—It is my privilege to open this meeting as Chairman. As your Chairman of the Council will deal with the operations of the year, I should only vainly take up your time in touching upon the subject myself. I have here a letter from Lord Graham, our President, whose place I am unworthily filling, and he says he very much regrets that owing to his duties he is unable to attend. Well, I have known Lord Graham for many years, and all of you know as well as I do that he is a man continually occupied in service duties, and takes a great interest in his war work. I think we are all very proud that we have such a President who is so occupied, much as we regret his absence to-day.

"DEAR MR. SANDBACH PARKER,—It is with sincere regret I write to say that on account of service duties I am not able to attend the First Annual Meeting of the British Empire Producers' Organisation. I rejoice to think of the great progress we have made, and in view of the short time of our existence it is really wonderful. We have been much encouraged by the recent union with us of the British Engineers' Association, representing about 500 engineering firms, and also by the affiliation of the Union of South African Industrialists. Our Organisation now embraces producers in every part of the Empire. We have support from India, Africa, Australia, Canada, and many lesser Dominions, but one and all enthusiastic in the cause that must weld British industry and production into a world-commanding influence. We must continue our work unceasingly, and make the B.E.P.O. known in every corner and workshop of the Empire; so much so that it will come to be a disgrace for any producer of British goods to stand without our gate. Wishing the British Empire Producers' Organisation every possible success in the new year of work, and with renewed expression of regret at my absence."

I also have letters of apology from Major-General Sir J. Newton Moore and Mr. H. Crum-Ewing. Now, I have suffered a great deal for many years from speeches of other people, which are generally much longer than I wish, and I will take care not to inflict upon you that which I do not myself gladly suffer. So I will take my seat and make way for the next item on the programme. I will call upon the Chairman of the Council to report upon the work of the Organisation up to the period ended April last.

Mr. C. SANDBACH PARKER (Chairman of the Organisation)—Sir John Rees and Gentlemen,—This is the first

Annual General Meeting of our Organisation, and I am sure you will expect me to devote a little time to a statement describing its formation and growth. It is sometimes mentioned in an almost critical tone that we were at the outset identified with one great industry. So far from feeling obliged to defend our origin, we have every reason now to regard it not merely with complacency, but with enthusiasm. Sugar was in at the beginning. Sugar was the industry that first rebelled with any real force against going back after the war to business as usual with Germany. Sugar was also the industry that for the first time in our history organised itself on an Empire basis. In the latter part of 1915 a draft form of contract for dealing in German beet sugar after the war was going the round in Mincing Lane. This came to the knowledge of Mr. Charles McNeil, to whose energy this great Organisation owes its inception. He felt that any return to trade with Germany after the war was a danger to be vigorously opposed, and with the energy and force with which we his colleagues on the Council and Executive Committee are now very familiar, he set to work to prevent it. He sought the help of a few friends in this country, Sir George Makgill, now our enthusiastic and hard-working General Secretary, Mr. V. A. Malcolmson, the Honorary Secretary of our Agricultural Section, Sir Edward Rosling, first Chairman of the Organisation, Mr. Paterson and Mr. Souchon (Mauritius), Mr. Clark (the Royal Mail Steam Packet Company), and Mr. Robert Kerr, who advanced £350 to finance the undertaking. Mr. McNeil at once set the cable to work to obtain the support from our Overseas Dominions, with the result that Messrs. E. Saunders (Leuchars and Fowler), representing the Sugar Planters of South Africa, and Mr. G. H. Pritchard, representing the Australian Sugar Producers' Association, were deputed by their associations to attend a conference of sugar producers. Sir Edward Rosling, the Chairman of the Anglo Ceylon and General Estates Company, was elected Chairman of the Organisation. On the arrival of Messrs. Saunders and Pritchard, the West India Committee was approached through Mr. R. Rutherford, then Deputy, now Chairman of that Committee, which in the past had been mainly responsible for advocating the interests of British cane-sugar, notably by the formation of the Anti-Bounty League in 1898, and whose efforts resulted in the abolition of sugar bounties by the Brussels Convention in 1902. The West India Committee, which in 1914 had desired to form a British Sugar League for the purpose of advocating the development of Empire-grown sugar, but had been urged in high quarters not to move in the matter at that time, decided, in view of this Organisation having already been formed, to support it, and nominated four members to represent their interests, of whom I was one. We were fortunate, again largely by the energy of Mr. McNeil, in enlisting the support of the Right Hon. W. M. Hughes, Prime Minister of Australia, our first patron, whose triumphant return to power after a hotly-contested election we cordially welcome. He opened the Conference of Sugar Producers of the Empire, composed of representatives of every sugar-producing country in the Empire, on May 8, 1916. Shortly afterwards Sir Edward Rosling was compelled, owing to pressure of other work, to resign the chair, and the Organisation did me the honour of electing me his successor. The Conference sat daily, and drew up a series of recommendations for the rapid development of the sugar industry in England and the Overseas Possessions, which were presented to Mr. Hughes before he left to attend the Paris Economic Conference, received his approval, and were laid before His Majesty's Government by a strong deputation introduced by Mr. Hughes on June 21. These are still under consideration, and we hope that the Government may shortly see fit to let us know whether they are prepared to adopt them. From the above you will realise the important part which sugar played in the early work of the Organisation, and justly so, because when war broke out we in this country were dependent upon foreign sources for over 96 per cent of our supply, and had for years been paying to Germany

and Austria some £15,000,000 annually for this essential food, which is also the raw material for some of our important secondary industries.

The scope of the Organisation was never limited to sugar, but was intended to embrace and link up all the industries of the Empire, both producing and manufacturing, in the belief that, in relation to State administration and to general commercial system, it is not good for an industry to be alone. In our view it is the principal motive of this Organisation to develop that sense of interdependence and mutual support so that there may be a fully and practically sympathetic understanding between those whose capital or whose labour is engaged in one British industry and those whose interest is in another, and again between the general industrial community of one part of the Empire and the rest. I think you will agree with me that the need of such an Organisation has been more than justified by the support which up to date we have received, with which I shall deal shortly. Having formed our Sugar Section, which did excellent work in producing a practical scheme within a short space of less than one month, we proceeded to deal with other industries on the same lines. We formed sections of Sugar Machinery Manufacturers, Agriculture, under the chairmanship, until he was called to the Cabinet, of Lord Milner, and Fertiliser Manufacturers, and were further strengthened by the affiliation of the British Electrical and Allied Manufacturers' Association, comprising some 150 firms, whose active support, financial and otherwise, has been of the greatest assistance to us in our work. To these we have to add more recently affiliations of the South African Federated Chamber of Industries, comprising 42 producing and manufacturing industries in South Africa, the United Planters' Association of Southern India, comprising 13 separate associations, the Indigo Planters, the Ceylon Association, and the Rubber Growers' Association, comprising 489 companies and 278 individuals. We have received the cordial support of the Associated Chambers of Manufacture of Australia, the Canadian Manufacturers' Association, and the Chamber of Agriculture of Mauritius, and are daily increasing our following in the British West Indies through the hearty co-operation of the West India Committee. So much for our overseas support. We have also to record important affiliations in this country, viz., the British Engineering Association, comprising about 500 firms, the Cable Makers' Association, comprising 14 firms, and the Liverpool Toy Association, a young industry to which we wish all success. I think therefore, gentlemen, we may fairly claim to be to-day the largest and most widely representative Industrial Association in the British Empire, or, indeed, the world.

I will now deal with our methods of working. From the first we realised that to be successful we must be really representative, and we adopted the principle which has been strictly adhered to, except temporarily in the case of agriculture, of admitting to membership only representative industrial associations. This principle of our constitution has received general approval. We are genuinely and strictly an association of associations. We believe that every productive trade should have its own association, and that it should govern its own affairs in the common interest of its membership. But, as I said before, it is not good for any trade to stand alone. There are other trades to which it sells; there are other trades from which it buys; and one of our objects, which will naturally be more conspicuous when peace returns, is to provide common ground for negotiations and adjustments which should further the conclusion of highly important new conventions and new methods. We felt that by adopting this course we gained in two ways: (1) We were able to voice the considered opinion of those industries expressed through their associations; (2) we reduced the area of discussion in our Committee to a minimum. We are conscious that by so doing we progressed more slowly, but each step was sure, and marked a definite and practical advance. We have recently formed an Associates Section

in order to enable individuals who sympathise with our objects and desire to support and take part in our work to do so.

We now come to our aims and objects. Though these are familiar to most of you, I think it well to emphasise two in particular, namely (1), to promote and foster production, manufacture, and trade throughout the British Empire with a view to rendering it self-supporting; (2) to ensure that each industry shall formulate its own fiscal policy, subject to the following condition—that wherever the introduction of import or export duties is demanded by any particular industry, such duties shall embrace the principles laid down in the resolutions passed at the Paris Conference, and shall secure Empire Preference, differentiating further between allied, neutral, and enemy countries. Dealing with labour, I would draw special attention to the resolution passed by our Council on September 2nd, which is an integral part of our policy, namely: "This Organisation places it on record that a cardinal point of its policy is the development of the Empire to render it self-supporting, and that the adoption of Preferential Treatment for the products of agriculture and industry is essential to this end. It further places on record as a principle of policy that Labour is entitled to its full share of any benefit which may be obtained through preference being given to any industry, and is prepared to give its support to legislation which has for its object the mutual interests and harmonious working between Capital and Labour with a view to the development and general good of the State. It is opposed to any form of preference which does not recognise the claim of the workers to a full and fair share of the advantages which such measures may secure."

I now come to the means by which we think our objects of a self-supporting Empire can be attained. I should at once explain that in aiming at the Empire becoming self-supporting, we fully realise the importance of commerce and overseas trade between the Empire and foreign countries. We believe that by developing the natural resources and productive power of our Empire to the utmost we shall concurrently bring about an increase in our trade with foreign countries. While we have most of what we want within our Empire, we have much that foreign countries want and have not got. We desire to promote the most friendly reciprocal relations between the Empire and our Allies first, and then with neutrals. With enemies we desire to cut off for a generation all trade relations. In years to come, when the horrors of the present war are mellowed by time, and a new generation has grown up free from the malign influences which have for the past forty years menaced the peace of the world, we can again consider to what extent we can resume trade relations with those countries; but I hope and think that no weak-kneed sentimentality will induce the people of the British Empire or their Governments to consider for one moment the resumption of trade with the present generation of Germans whose black record of crimes in this war has blasted for ever their claims to civilisation and the brotherhood of nations. Gentlemen, war is a terrible necessity, but war conducted as our enemies have conducted this war can never be forgotten or forgiven until those responsible have ceased to cumber the earth, and a new, and we hope more civilised, generation has taken their place.

Since the Organisation was formed we have received much help from the members of the Government, Ministers of the Dominions, and other prominent men who have addressed meetings on our behalf, and to whom I tender the thanks of the Organisation: The Rt. Hon. W. M. Hughes, Prime Minister of Australia; The Rt. Hon. W. F. Massey, Prime Minister of New Zealand; The Rt. Hon. Sir Edward P. Morris, Prime Minister of Newfoundland (all of whom are patrons of the Organisation); The Rt. Hon. Sir George Foster, Minister of Trade and Finance, Canada; The Hon. R. Rodgers, Minister of Public Works to the Dominion of Canada; Sir Thomas

Mackenzie, High Commissioner for New Zealand; Sir Joseph Ward, Finance Minister New Zealand; Viscount Milner, Member of the Imperial War Cabinet; The Rt. Hon. Walter H. Long, M.P., Secretary of State for the Colonies; The Rt. Hon. John Hodge, M.P., Minister of Labour; The Rt. Hon. Austen Chamberlain, M.P., Secretary of State for India; Sir James Meston, K.C.S.I., Member of the Imperial War Cabinet; Sir Owen Philipps, K.C.M.G., M.P., Chairman of the Royal Mail Steam Packet Company; and Sir J. D. Rees, K.C.I.E., M.P., who is at present in the chair. Our fortnightly luncheons, inaugurated on February 22nd, when Mr. Massey was our guest and the Marquis of Graham took the chair, have, I think you will agree, been an unqualified success. Our average attendance has been about 140, and while the allotted time of one hour has been slightly exceeded, the importance of the speakers and the fact that practically no one has ever left before they had finished testifies to the interest taken in our movement.

The summons to the War Conference and Cabinet offered an opportunity for pressing our views with regard to the development of the Empire and the carrying into effect of the Paris Economic Conference resolutions on the Government of this country sitting in council with the representatives of the Dominions. We drew up a memorial urging immediate action in this direction which was signed by no less than 84 representative industrial associations in this country and all parts of the Empire representing immense and widely distributed interests. We had good reason to hope that we should have had an opportunity of presenting it to the War Cabinet by a deputation which Mr. Massey had promised to introduce, but ultimately this had to be abandoned owing to pressure of work and lack of opportunity. The memorial was, however, sent to all the members of the War Cabinet and Conference, and, we believe, was not without influence upon the decision of those bodies, recently made public, to adhere to the policy of Imperial Preference and to carry into effect the resolutions of the Paris Conference. That decision is now the accepted policy of Great Britain, India, and all the Dominions except Australia, which was, unfortunately, owing to the general election there, not represented, but there is every reason to believe that she will fully concur. It is the policy which this Organisation has consistently advocated from its inception, and in our opinion is the only policy which can bring about the development of production within the Empire which all members of the Organisation ardently desire and are working to achieve. The memorial, I have no doubt, was by far the most influential document of the kind ever laid before any Government, and without in any way wishing to detract from the value of the efforts of other bodies working for the same object, we may legitimately express our satisfaction that the main planks of our platform are now the accepted policy of the Governments of the Empire. This definite pronouncement of policy by the Government of the United Kingdom marks the greatest revolution in the conditions of the world's commerce known to history, and we may now feel that the future welfare of our Empire is assured. But our work as an Organisation has only begun. Now that the policy is accepted the details have to be worked out and a system evolved, in which we hope to be of practical assistance to the Government, and it will be our duty to press upon them the necessity of immediate action to give effect to their decision. We have already addressed a letter to the Prime Minister urging that our recommendations with regard to sugar, which involve no fresh legislation, may at once be adopted and put into operation.

With regard to our other activities, I will only indicate the lines on which we are proceeding. (1) Agriculture: Our Agricultural Section drew up an interim report which we presented to the Government, dealing with the most urgently pressing agricultural problems. This section has been reconstituted to represent the chief agricultural bodies in the United Kingdom, and it is hoped to secure the support of similar bodies in the Overseas Dominions.

The executive committee of the section will at once proceed to deal with the programme of questions for consideration originally laid down, which cover a great number of important subjects on which it is necessary that the representative views of the associations composed of men actually engaged in the industry should be formulated and expressed to the Government. (2) Publicity Department: We have established a Publicity Department under the able guidance of Mr. T. C. Elder, which we hope will in due course be self-supporting. The object is to give publicity by advertisement and otherwise to the wants of industries, not only in the Empire, but in foreign, other than enemy, countries and the sources within the Empire from which they can be supplied. In this connection we are working in consultation with the British Association of Trade and Technical Journals, which has affiliated with us and which numbers about 150 well-known trade journals in this country. We hope very shortly to show substantial progress. (3) Education Committee: We have a strong Education Committee engaged in considering the question of greater facilities for research work and the training of young men for special industries, notably tropical agriculture, and we hope also to secure the co-operation of an important Education Committee which has already been dealing with the question of engineering education, one of the sub-committees of the British Electrical and Allied Manufacturers' Association. (4) We have been fortunate in securing for one year from May 1st the services of the Hon. F. M. B. Fisher, ex-Minister of Trade and Marine in New Zealand, who has already addressed several meetings and done good work for us, for which I desire on behalf of the Organisation to tender him our grateful thanks. He will be in charge of the arrangements of meetings, in order to educate the public mind on our policy. Those who have been privileged to hear Mr. Fisher on the platform will agree that we are indeed fortunate in obtaining the services of so able an advocate. (5) Journal: It is proposed to institute a journal of the Organisation in extension of the monthly reports.

There is only one more point that I wish to emphasise, viz., the necessity of this Organisation co-operating with kindred associations who are working for the same object and are prepared to accept our policy. I have on every opportunity, both public and private, urged this upon those engaged in similar work, and I am glad to record that since January last we have had a joint committee with the Federation of British Industries, which is ably presided over by Mr. Dudley Docker. May I venture to hope that the declaration of policy by the Government will enable them to see their way in the near future to a still closer working arrangement? In conclusion, gentlemen, I wish to express my personal gratitude to all my colleagues and the officers and staff of our Organisation for their support, assistance, and forbearance to me in the execution of my duties as Chairman. But for their enthusiasm, energy, and devotion the Organisation could not have achieved the results of which we are to-day so justly proud, and I know that we can rely upon their continuing to further our work with equal energy in the coming year. More I cannot say, nor could we wish. It has been a real pleasure to work with such assistance for so great a cause. I thank you, gentlemen, for the patient hearing you have given to me in a statement of necessity rather long, but I hope not without interest on the occasion of this our first annual meeting, and I beg to move "That the balance sheet and accounts be accepted." (Applause).

CONJOINT BOARD OF SCIENTIFIC SOCIETIES.

THE fourth meeting was held at the Royal Society on June 13, Sir JOSEPH J. THOMSON, O.M., Pres.R.S., in the Chair, to receive the report of the Executive Committee on the work of the previous six months.

As the Report indicates, a number of important questions of scientific and industrial importance has occupied the attention of the Board.

Various bodies are at present interested in the formation of a census of the mineral resources of the Empire. It was agreed to enter into communication with these bodies, and to make suggestions with a view to the publication of information in a form useful to the general community.

Interim reports were received and approved on the necessity for an anthropological survey of the British people, on the best methods for carrying on the International Catalogue of Scientific Literature, and on an enquiry into the desirability or otherwise of the adoption of the metric system throughout the British Isles.

The Sub-Committee on National Instruction in Technical Optics reported that a scheme approved by the Board of Education had now come into operation. Under the ægis of the Imperial College of Science and Technology an Advisory and Administrative Committee had been formed to organise instruction, and Mr. F. J. Cheshire, a member of the Sub-Committee of the Board, has been appointed Director of Studies in Technical Optics. Although the President of the Board of Education did not see his way to adopting the suggestions of the Sub-Committee, the Board heard with satisfaction that a promising effort has been made to solve a question of considerable national importance.

A Sub-Committee, having considered special cases of magnetic disturbances revealed by a magnetic survey of the British Isles and their possible connection with the occurrence of iron ores, recommended a detailed investigation of two test areas, in order to ascertain how far, under the conditions of British iron ores, the magnetic survey was likely to prove of economic value. Arrangements for carrying out the investigation are in progress.

An Agricultural Sub-Committee, with the Earl of Portsmouth as Chairman, reported that it is at present devoting itself mainly to engineering questions. It is engaged in collecting information with regard to the transport of raw materials to farms and agricultural products from them, to the power required for this purpose, and for seasonal operations on the land, with a view to comparing the relative advantages and costs of steam or internal combustion engines and electrically operated machines. It is dealing also with the possibility of co-operation in repairs and skilled labour, and is considering the various types of tractor most suitable to large and chiefly arable farms, and to moderate sized mixed farms, having regard to the different local circumstances and requirements.

A Sub-Committee was nominated to report on what is at present being done to ascertain the amount and distribution of water-power in the British Empire.

A complete report of the first year's work of the Board will be published in due course.

NOTICES OF BOOKS.

An Investigation of the Coals of Canada. Extra Volume, Supplementing Report, No. 83. *Weathering of Coal.* By J. B. PORTER, E.M., Ph.D., D.Sc. Ottawa: Government Printing Office. Pp. xii+194+xxiii.

THIS monograph contains summaries of the work of the author and others upon the weathering of coal, and by comparing various results and examining the many statements which have been made upon the subject the author has succeeded in bringing some important facts to light. The general causes of weathering are first discussed in some detail, and it is shown that different coals show very great differences in their liability to weather. Then the practical problem of how to prevent or minimise the weathering of stored coal is considered, and suggestions are made as to the precautionary measures which may be adopted to ensure safe storage. For example, the elimination of dust by screening has been found to be

beneficial, and shallow piles are much safer than those of a depth exceeding, say, 8 or 10 feet. Treatment with a solution of calcium chloride has been found a successful means of preventing fires, and it is said to be cheaper than ventilation by perforated pipes, which is, on the whole, the most satisfactory method.

CORRESPONDENCE.

VOLUMETRIC DETERMINATION OF SULPHUR IN PYRITES.

To the Editor of the Chemical News.

SIR,—Dr. Craig in his interesting and instructive article, "The Volumetric Determination of Sulphur in Pyrites" (CHEMICAL NEWS, cxv., 253, 265), remarks on desirability of a reliable and fairly rapid method for this purpose. With your permission I will describe a plan (so far unpublished) in use by me in 1872—4 in Manchester.

A solution of sulphuric acid is made up of which 1 cc. = 0.01 grm. of sulphur along with 1 of barium chloride to correspond. To find the exact "titre" of the BaCl_2 , run 49 cc. of the acid into a flask, add 5 cc. of HCl and 150 of hot water, and bring to the boil. Now run in 48 cc. of the BaCl_2 , boil up, and remove flask to bench, let stand, and filter 5 cc. through small paper into a marked test-tube, and add 2 drops of the BaCl_2 . If a precipitate appears at once return solution and washings of filter to flask and add cautiously more BaCl_2 .

(NOTE.—The "end-point" of the reaction is the absence of any cloudiness in 5 cc. of the hot filtrate on addition of 2 drops of the BaCl_2 after three minutes repose. A sand-glass was used for timing).

Should the solution remain clear the operator may find he has just hit the "end-point" or has slightly over passed it. He will now filter a further 5 cc., and test by addition of 2 drops of the acid. In case a cloudiness should appear he will return the contents of both test-tubes and washings of filter to the flask, read off both burettes, and go back with drops of acid until the "end-point" is found; i.e., until 2 drops of either reagent ceases to give a cloudiness under the given experimental conditions. With a little practice it is easy to hit off the end-point.

Agreement established between the solutions in terms of sulphur the operator may now weigh out 1 grm. of very finely ground pyrites, oxidise in flask, drive off all HNO_3 , and proceed as above described. It is well to keep the experimental conditions the same as the volume of liquid.

Should the analyst know from previous deliveries that he is dealing with high-grade Spanish ore holding 48.4 to 49 per cent of sulphur, he will run in 47 cc. of BaCl_2 right away, and then proceed by $\frac{1}{2}$ cc. at a time, boiling up, and filtering off 5 cc. after each addition. I have not had occasion to use bromine to complete oxidation of minute particles of free sulphur, but as Dr. Craig points out when HNO_3 alone is employed there may be incomplete oxidation for which a few drops of Br is the remedy.—I am, &c.,

HARCOURT PHILLIPS.

Court Chambers, Bolton, Lancashire.

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